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Analysis of a New Cleaning Technology Based on Supercritical Carbon Dioxide Pre-treatment for Diesel Engine Remanufacturing

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by

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Abstract

Remanufacturing is the rebuilding of a used product to at least its original performance with a warranty that is equivalent or better than that of the newly manufactured product. It is a vital means in improving manufacturing sustainability, through saving raw materials, reducing carbon emissions and conserving product commercial values. As the one of the demanding steps in remanufacturing process, cleaning is also one polluting stage because of the use of environmental detrimental cleaning agents and the large amount of energy consumptions. The specific aim of the work demonstrated in this thesis is to find an alternative cleaning agent that could achieve the effective cleaning of decommissioned engine parts, in an environmentally greener way. More generally, the study in this thesis uses supercritical carbon dioxide (SC-CO_2) as the green agent to reduce the possible environment loads induced by conventional cleaning technologies and further investigate the feasibility of this method in removing other contaminants as an application extension.

Organic contaminants, containing greases, lubricating substances and carbon depositions are the most commonly observed contaminants in a decommissioned engine, and they are analysed by a series of analytical methods to validate the feasibility of SC-CO_2 cleaning in this study. Experiments on grease, lubricating oil and paint coatings cleaning are carried out on the supercritical fluid (SCF) facility with the addition of liquid blasting to remove residues after SC-CO_2 treatment. A new cleaning method combining SC-CO_2 pre-treatment and liquid blasting post-treatment processes is proposed and a comparison is conducted between this method and conventional method (thermal decomposition and shot blasting

cleaning). Operation parameters for liquid blasting process are determined through single particle blasting test and the comparison demonstrates the new method has a minimal impact on the surface properties of substrate materials, while the conventional cleaning method has a significant negative impact.

Ultimately, the comparative life cycle assessment between two methods demonstrates the new cleaning technology can attain a higher cleanliness with better environmental performances. It is concluded that the SC-CO_2 cleaning could provide a “cleaner production” method for remanufacturing.

Publications

Journal Papers

1. **Li, M**., Liu, W., Short, T., Qing, X., Dong, Y., He, Y. and Zhang, H.-C. (2015) 'Pre-treatment of remanufacturing cleaning by use of supercritical CO_2 in comparison with thermal cleaning', Clean Technologies and Environmental Policy, 17(6), pp. 1563-1572.
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Conference Papers

5. Liu, W., Zhang, B., **Li, M. Z**., Li, Y. and Zhang, H.-C. (2013) 'Study on Remanufacturing Cleaning Technology in Mechanical Equipment Remanufacturing Process', Re-engineering Manufacturing for Sustainability: Springer, pp. 643-648.
6. Liu, W., Qing, X., **Li, M.,** Liu, L. and Zhang, H. (2015) 'Supercritical CO_2 Cleaning of Carbonaceous Deposits on Diesel Engine Valve', Procedia CIRP, 29, pp. 828-832.

Contents

Nomenclature

Symbol	Definition	Units
$[C_f]$	Concentration in the fluid	mol/m^3
$[C_S]$	Concentration on the surface	mol/m^3
C	Concentration	mol/m^3
D	Diffusion coefficient	cm^2/s
EF	Equivalence factor	—
EP	Environment Potential	—
f	Frequency of the pump rotor	Hz
I_n	Inventory/Original data	—
O_m	Result of environmental impact category m	—
P	Partial coefficient	—
PC	Critical pressure	MPa
Q	Outflow rate	ml/min
Q	Amount of emission or resources	—
R	Gas constant	J/(mol·K)
S_m	Sensitiveness measuring the Om variation with the change of I_n	—
T	Temperature	K or ℃
T_C	Critical Temperature	K or ℃
T_f	Melting point of solute	K or ℃
V	Molar volume	m^3/mol
x	The levels of the independent variables	—
x	Mole fraction	—
y	Response caused by parameter variations	—

β	Constant regression coefficients	—
ΔH_f	Heat of fusion	J/mol
Δi_n	Variation quantity of I_n	—
ΔO_m	Variation quantity of O_m	—

Abbreviations

ANOVA	Analysis of variance
AP	Acidification potential
CFC	Chlorofluorocarbon
DBE	Dibasic esters
DoE	Design of experiment
DUT	Dalian University of Technology
EDS	Energy dispersive spectrometer
EPMA	Electron probe micro-analyser
FTIR	Fourier transform infrared
GWP	Global warming Potential
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact analysis
LQB	Liquid blasting
MEMS	Micro-Electro-Mechanical System
NMP	N-Methyl Pyrollidone
ODS	Ozone depleting substances
OEM	Original equipment manufacturer
PPC	Pulse Pressure Cleaning
RDP	Resource depletion potential
RI	Respiratory Inorganics
SC-CO_2	Supercritical carbon dioxide

SCF	Supercritical fluid
SEM	Scanning electron microscope
TEM	Transmission electron microscope
THD	Thermal decomposition
VOC	Volatile organic compounds
WEP	Water eutrophication potential
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1

Introduction

1.1 Requirement for Sustainability Development

The expansion of manufacturing industry over previous decades has seen environmental issues, caused by scrapped equipment, become increasingly serious. Sustainable development and resource shortages, combined with legislative pressure, have brought this to the attention of the world (Liu et al., 2014, Singh et al., 2014). However, the pace of manufacturing development cannot be consequently stopped, as it is the pillar of the economic development. Researchers all over the world are now committed to exploring new manufacturing paradigms to change the current situation.

Mineral resources are the foundation for machinery and equipment in the manufacturing industry; yet, the global lack of mineral reserves has become its main restriction. In China, for instance, almost 80% of raw materials are depended on the mineral industry but there has been extreme poverty of ores like copper, aluminium and iron (Chen, 2012). From the Mineral Commodity Summarizes 2017 by the U.S. Geological Survey (Ober, 2017), the reserves of copper, iron and aluminium ore are 0.6, 160 and 61.2 billion tons respectively and are being consumed at the rate of 15.5 million, 2.24 billion and 400 million tons per year.

Resource depletions could be foreseen if we do not take measures to change the current situation. In this circumstance, the concept of sustainable manufacturing came into being, which could reduce dependence on raw material. From an engineering perspective, sustainable manufacturing should minimise its reliance on natural resources and cycles to ensure that the new mode does not lead to diminished quality of life due either to losses in future economic chances or over use of natural resources (Mihelcic et al., 2003). Sustainable manufacturing emphasises reductions and source control at the original manufacturing stages (reduce), along with the reuse, remanufacturing and recycling (3Rs) of decommissioned products or their components with residual values. Remanufacturing, among the 3Rs, is the ultimate form of recycling (Giutini and Gaudette, 2003).

1.2 Remanufacture

Researchers have been seeking a comprehensive definition for remanufacturing over the past decades and until very recently an unambiguous definition has been accepted by the academia and industry. Remanufacturing is a series of manufacturing steps acting on end-of-life products to return them to at least OEM (original equipment manufacturer) original performance specifications from the customers' perspective and giving the resultant product a guarantee that it is at least equal to that of a newly manufactured equivalent (BSI, 2009, Ijomah, 2002). Remanufacturing is a crucial procedure in sustainable manufacturing and the circular economy, beginning with the reclamation of durable decommissioned products. These products, which are typically called "cores" (Nnorom and

Osibanjo, 2010), still possess residual values from original manufacturing, as failures usually happen on just some parts rather than the overall equipment. Through remanufacturing, products' additional values obtained from OEM could be optimised and avoid energy and material wastes due to disposal and scrapping. Consequently, remanufacturing can reduce capital investment and material and energy consumptions and provide crucial technological supports of the circular economy (Boustani et al., 2010).

1.2.1 Differences between Remanufacturing and Other 'Re-'s

There are many terminologies related with the prefix 're' in Sustainable Manufacturing, e.g. repair, recondition, refurbish, restore and reuse. Remanufacture is distinct from other terms in its process and positioning within the material flow loop (Gray and Charter, 2007). One distinction that should be specifically mentioned is that the performance of remanufactured products should be over or at least equal to the OEM's original performance specification (Ijomah, 2002). Among all these processes, remanufacturing is more environmentally preferable (BSI, 2010).

To maintain the original performance level (Abdulrahman et al., 2014, Ijomah, 2009) and be equal to the new product warranty (Ijomah et al., 2007), the cores (which has been defined in the first paragraph in Section 1.2) must go through specific remanufacturing processes. In comparison with repair, remanufacture is applied on all retired products rather than only defective ones. Fig. 1.1 (Liu et al., 2014) gives a basic flow chart of remanufacturing procedures whereas steps used in practical operations are specified accordingly. Cores are primarily collected

from relative industries and shipped to remanufacturers. In a basic remanufacturing procedure, cores are initially cleaned, as a preparation process prior to disassembly, to obtain a satisfactory cleanliness, which guarantees an acceptable working environment for the workers' health. Parts with apparent defects are scrapped and recycled into raw materials for future manufacturing process. In a remanufacturing process, this could only happen when added values are exhausted or the input of remanufacturing them outweighs their actual values. Usable parts are inspected and categorised into remanufacturable, non-remanufacturable and intact components, going through remediation, scrapped and directly into reassembly, respectively. Tests are carried out on the remediated parts, prior to reassembling, to ensure that all parts from the previous procedure are reliable for the normal operation. Tests after reassembly are operated using the same criterion of OEM products to guarantee an equal or even higher warranty in comparison with the original. All manufactured products should be painted, packaged and certified based on corresponding industry standards.

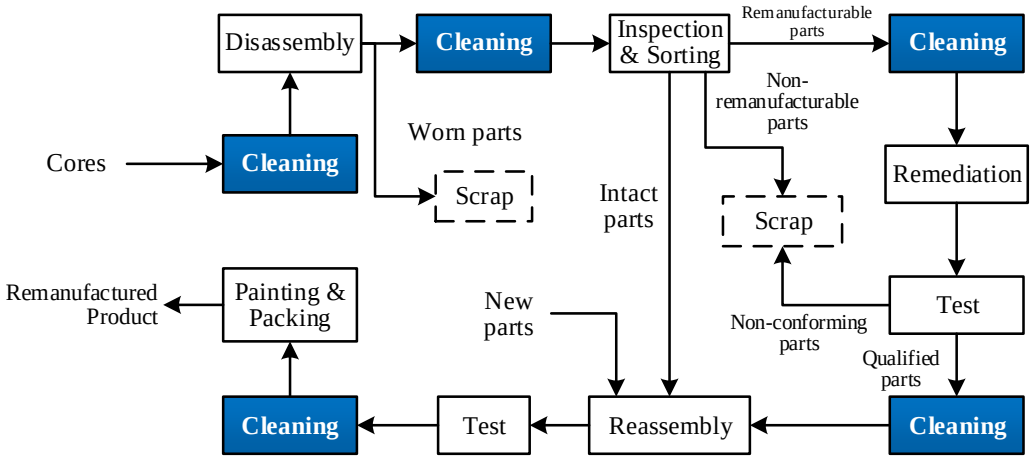

Fig. 1.1 Basic technological process of remanufacturing

1.2.2 Significance of Cleaning in Remanufacture

Remanufacturing comprises a series of technological steps, of which cleaning is one of the most demanding, notwithstanding the limited attentions from researchers. In remanufacturing, cleaning is generally the process where decommissioned, contaminated parts are cleaned prior to dimensional restoring or related remediation, reducing pollution status until a designated cleanliness is reached (Liu et al., 2013, Long et al., 2014). Compared with the OEM, cleanliness requirements become more specific in remanufacturing, as cleanliness requirement for one 're-' operation always differs from that of another one. In addition, contaminating conditions vary for different equipment types, even those apparatus are of a same model and type, because they are retired from different environments (Seitz, 2007). Even though cleaning is an auxiliary operation between other processes and has not received enough concerns, it is still of great significance in many industries for the subsequent operations (Kikuchi et al., 2011). Considering the inspection and sorting step, for example, cores must already be clean enough for the apparatus to detect invisible defects in the naked eyes, ensuring it is suitable for the subsequent steps. Cleanliness directly determines the success of some specific processes during remanufacturing, as well. One typical example is the dimensional restoring of centrifugal compressor blades, whose edges are often worn due to ablations and frictions. During this process, contaminating particles on the damaged surface could transform into internal slag or inclusions, which could dramatically reduce service life of one remanufactured compressor (Zhang et al., 2015).

Cleaning is an auxiliary process between different stages; consequently, it is

one of the most demanding in remanufacturing. However, the pollution generated from this stage cannot be ignored before remanufacturing really becomes an environmentally favourable “end-of-life” treatment method, refreshing retired products into a like-new condition (Hatcher et al., 2014). To remove contamination from core surfaces, the cleaning process is time consuming and labour-intensive (Chang et al., 2013, Sakai, 2007). Moreover, traditional cleaning methods use organic materials or chemical agents to achieve satisfactory cleanliness (Lindahl et al., 2013), which are usually detrimental to the environment and workers health, leading to an environmental problem.

The development for sustainable manufacturing cannot compromise with the defectives induced by these environmentally unfriendly perspectives. To meet “the needs of the present” (Brundtland, 1987) and guarantee the continuous development and growth, there are very strong demands to explore new approaches, which are environmentally benign, to overcome the drawbacks described above, especially in the remanufacturing cleaning aspects when considering its great demand.

1.3 The Thesis

Cleaning operations that impart product surfaces required cleanliness are among the most polluting activities in manufacturing (Williams, 2008). Currently, a variety of solvents, such as carbon tetrachloride, trichloroethane and petroleum distillates, etc. have been used in cleaning operations, to attain a good result. However, these solvents are usually detrimental to the environment. Consequently, research has considered decreasing or terminating the use of those solvents,

improving the recovery rate of aqueous cleaner and targeting the sustainable development of closed-loop manufacturing industry (Rajagopalan et al., 2001). Considering the increasingly serious greenhouse effect worldwide, there is also an urgent requirement for carbon reduction. One way of combating these problems would be taking advantages of carbon dioxide as solvents to replace those traditional organic substances. If the greenhouse gas could be kept within a closed-loop, problems of both the greenhouse effect and flaws of using chemical solvents would be settled.

1.3.1 The Research Hypothesis

Remanufacturing was initiated three decades ago (Lund, 1983, Kutta and Lund, 1978), primarily focusing on the recycling of automobile components in automotive industry (Seitz, 2007). Over almost three decades of development, remanufacturing has involved many industries, e.g. the automobile, the metallurgical equipment, the aerospace field and the electronic equipment (Hashemi et al., 2014). Even in the current trend, researchers and manufacturers are still paying much more attention to large equipment because its residual value added by OEMs would be far greater. Current remanufacturing studies mainly focus on the motivations and barriers (Wei et al., 2015), environmental impacts (Kim et al., 2008, Zhang and Chen, 2015), reverse logistics (Chan et al., 2012), related economic perspectives etc. rather than on technologies for practical operations, owing to the variety of decommissioned products and their different conditions.

For example, a commonly used cleaning method for cleaning retired diesel

engine parts was to use thermal decomposition to vaporise or combust oily compounds (Erwin, 2017). This method is always detrimental to the environment because a large amount of fuel is used in the thermal decomposition operation. Therefore, the requirement of proposing an alternative method replacing thermal decomposition is of great significance. Target contaminants are oily and organic compositions which broadly exist on and inside decommissioned engines. The study focused on using supercritical CO_2 as the solvent, which are environmentally benign or friendly, to remove contaminations from decommissioned engines. In contrast to the well-defined cleaning operations for OEMs, current methods for remanufacturing cleaning are basically experience-based originating from practical operations rather than knowledge-based selection of suitable methods according to scientific studies (Gray and Charter, 2007). Therefore, there are often problems such as low efficiency, environmentally detrimental or high-cost associated. Considering the situation, this thesis proposes a method that is highly efficient, cleaner and industrialisation accessible, to change the current state-of-the-art of remanufacturing cleaning. It can be therefore concluded that the hypothesis in this thesis is:

"The method proposed in this thesis is operable, efficient and greener comparing with conventional methods and the use of this method can retain the original features of components."

1.3.2 Research Impact

This research is primarily focused on exploring an alternative means for remanufacturing cleaning, which is expected to overcome the drawbacks of using

traditional methods and provide relative theoretical support for the removal mechanism in cleaning processes. Although the research originated from sustainable manufacturing, it potentially impacts on the academic community. These areas could include:

- Proposing the utilisation of supercritical CO_2 into cleaning of diesel engine remanufacturing operation and replacing the originally used thermal decomposition method;
- Expanding the scope of supercritical CO_2 utilisation into industrial application, which could significantly promote the CO_2 requirement and therefore reduce the greenhouse effect.
- Applications for the removal of other organic contaminants such as paint layers and furtherance of research into the mechanism differences between different contaminant types.
- Extending the application of supercritical CO_2 to the area of heavy organic contaminant layers; beneficial to surface treatment and coating areas.
- Providing references for proposing a convincing evaluation method for the core cleanliness in remanufacturing.
- Clarifying the approaches for improving supercritical CO_2 cleaning into a greener manufacturing method based on the life cycle assessment study surrounding different cleaning technologies.

1.4 Research Aim

The aim of this research is to propose new methods, which are environmentally sound or friendly, for the remanufacturing cleaning process, using supercritical carbon dioxide (SC-CO_2) to clean parts from decommissioned engines, to explore the optimal operation parameters for an ideal removal result. Supplemented by other post-treatments, the supercritical fluid cleaning will be assessed from the perspective of cleaning effectiveness, environment impact and energy consumption perspectives. Ultimately this research will provide an "greener" compound cleaning method for remanufacturing industry and further utilisation within the entire sustainable manufacturing industry.

1.5 Research Objectives

The research aim was achieved by accomplishing the research objectives stated as follows:

- Analyse the composition, physical structure and chemical properties of engine contaminations, considering the validity of the cleaning method proposed in the project.
- Design and assess a compound cleaning test bed to evaluate the efficiency of the supercritical fluid cleaning method.
- Use the cleaning test bed with the addition of theory of design of experiment to obtain performance data for parameter optimisation.
- Evaluate the environment impact of the newly proposed compound cleaning method using life-cycle assessment methodology.

1.6 Thesis Structure

The work outlined in the thesis is divided into eight chapters. Each chapter logically states progressions throughout the research and distinctive stages achieved. The thesis is divided into for main stages as follows:

1. Literature review and proposal of new cleaning agent (Chapter 1–3).

2. Contaminant analysis, feasibility demonstration of SC-CO_2 cleaning and process optimisation (Chapters 4 and 5).

3. Proposal of new, green cleaning technology and comparative analysis between the new and conventional technologies and expanding its application (Chapters 6).

4. Environment performance assessment between new and conventional technologies (Chapter 7).

The chapters in this thesis are arranged based on the progress of research so as to clearly present the integrated narrative. The research can be also considered as a feasibility study into broader applications of the green cleaning technology.

Chapter 2

Cleaning for Remanufacture

Cleaning methods used in remanufacturing operations are usually adopted from traditional cleaning industries. However, the core polluting conditions are diverse from one area to another. It is consequently necessary to have a comprehensive understanding of the current cleaning technologies in the remanufacturing industry. This chapter comprises a wide range of literature surrounding cleaning technologies of automobile (re-)manufacturing industries and gives the pros and cons of traditional and newly adopted technologies. Although these conventional technologies can meet the cleanliness requirement of subsequent operations, environmental issues from cleaning operations should not be ignored before remanufacturing can truly become a “green” and sustainable manufacturing mode. Critical elements in cleaning are summarised in this chapter, as well, for identifying a proper cleaning method with “green” properties.

2.1 Distinctions of Cleaning for Remanufacture

Industrial cleaning is the process of reducing unnecessary substances such as lubricating oil, machining residues and other impurities, which can prevent the normal use of one product, on or in a product and recovering its original function.

The diagram in Fig. 1.1 has highlighted the positions where cleaning

operations are often required. Cleanliness requirements are different at different stages and usually become stricter at the later stages in line with the quality standard of remanufactured product (Liu et al., 2013). Firstly, the cleaning processes prior to core disassembly are to reduce the contamination quantity on the external of products. Secondly, the cleaning at the detecting stages is for the convenience of identifying defects and damage such as surface abrasions, micro cracks and other failures, by removing contaminations of grease, scales, rusts, carbon depositions and paint layers adhering to the surface. This process guarantees the reliability for remanufacturing the cores and to determine the suitable remediation approaches. Moreover, cleaning operations at other stages, for instance prior to reassembly, painting and packing, are designed to remove contamination (oil, greases, machining residues, etc.) and ensure the required cleanliness of subsequent steps. Although cleaning operations are auxiliary processes to most manufacturers, they are playing a critical role in ensuring product qualities and ultimate performances. Inadequate cleanliness or inappropriate cleaning method would induce unacceptable production yields or even to the failure of one product within the normal service duration (Kauffman and Lee, 2013). In remediation operations, for instance, when using laser cladding in dimensional restoration, the contaminations on the damaged surface could transform into internal inclusions that reduce the service life of remanufactured products (Zhang et al., 2015).

Remanufacturing cleaning is distinct from cleaning in OEM and other “re-” modes in industry. In maintenance, cleaning targets at removing contamination on areas adjacent to damage as a preparation for repairing, while cleaning in

remanufacturing is carried out on the entire body of one product to attain the cleanliness requirement. Conditions for OEM cleaning are quite different from the polluting conditions of decommissioned products. Basically, in a new product manufacturing, cleaning objects are identical in dimensions and materials; also, targets for removal are identical, which are mainly cutting fluid residues, lubrication substances, antirust oil, and polishing pastes etc.. Remanufacturing cleaning deals with products retired from various working environments with different polluting conditions, materials and structures. These complexities increase the difficulties in batch cleaning for remanufacturing (Kauffman and Lee, 2013). Moreover, OEM cleaning has highly standardised cleanliness protocols (Hong and Day, 2013), such as the ISO Standard 16323, which has given comprehensive recommendations for cleaning in original manufacturing operations. Nonetheless, remanufacturing cleaning is facing the problems of lacking in relative cleanliness standards in each step throughout remanufacturing procedures. Current cleaning in remanufacturing is usually experience-based rather than systematic rules and standards. Therefore, there is still great potential for optimisation and innovations in changing the situations in remanufacturing cleaning. Further research into remanufacturing cleaning is therefore very essential.

In this Chapter, basic elements, traditional approaches and their pros and cons are summarised as the fundamental knowledge of proposing new technologies that are feasible for remanufacturing cleaning.

2.2 Basic Elements in Remanufacturing Cleaning

The removal of contaminants is achieved by means of mechanical, physical,

chemical or electrochemical interaction between the cleaning agents and the target contaminant. Through this process, greases, rusts, carbon depositions, paint and scales are detached from the core to obtain the specific cleanliness. In general, one remanufacturing cleaning operation includes four basic elements, namely the cleaning objects, target contaminants, the cleaning agents and cleaning forces.

2.2.1 Cleaning Objects

A cleaning object is the part that required a cleaning operation in remanufacturing. Here, the substrate material is a decisive factor that requires additional considerations when selecting a feasible cleaning technology. Machinery parts are usually made of metals such as steel, aluminium alloys, etc. while electronic components are primarily made of semi-conductor materials like monocrystalline silicon. The shape and geometric dimensions of one cleaning object could also affect the eventual cleaning performance. Diesel engine cleaning may encounter substrates such as aluminium, steels, brass products, copper materials, iron products and alloys of beryllium, brass, iron, magnesium, nickel and titanium. The cleaning of different component requires different cleaning methods.

2.2.2 Target Contaminants

Contaminants are the deposits formed due to long-term physical, chemical, physiochemical and/or biological interactions with external matters during the service period, or obtained from the manufacturing process for example residual metal cutting fluid etc.. Remanufacturing cleaning is a process of removing this contamination from the core to attain a specific cleanliness. In the cleaning of

engine components, the common contaminants are summarised in Table 2.1.

Table 2.1 Commonly observed contaminants in remanufacturing cleaning for a diesel engine product

Contaminant	Position	Material compositions	Features and characteristics
External deposits	External parts	Dust, oil sludge, etc	Easy to clean, but difficult to clean completely
Lubrication residues	The contact surfaces requiring lubricating medium	Oxidation and aging oil, water, salts, products of corrosion and deterioration	With complex compositions, furring, which determines corresponding cleaning methods.
Carbon depositions	Combustor surface, air valve, piston head and ring	Carbides, lubricating oil and tar, oxygen acid, ashes, etc.	Mostly insoluble therefore difficult to clean
Film-like painting	Piston skirt, connecting rod.	Carbon	Low strength, easy to clean
Other sediments	Shell wall, crankshaft journal, oil pump, filters, lubricating oil passage.	Lubricating oil, tar, carbides and ash contents, etc.	Most of the components are insoluble and difficult to clean
Scale deposit	Cooling system	Calcium and magnesium salts, etc.	Soluble in acid
Rust	The surfaces of component	Oxides of iron and aluminium, etc.	Insoluble in water and alkali but soluble in acid.
Detection residues	Randomly on the entire surface body	Metal debris and fingerprint, etc.	With minor adhesive forces, and easy to be removed.
Machining residues	The entire body surface	Metal debris, polishing paste, abrasives, lubricating liquid, coolant, etc.	Adhesive force is not large, but need to clean thoroughly.

2.2.3 Cleaning Force

One contaminant molecule is attached to other molecules or substrates through molecular interaction or electrostatic forces and therefore contaminants come into being. Cleaning forces in this process overcome these forces and strip

the contaminant layers off the substrate. In general, there are five kinds of cleaning forces exerted between cleaning objects, generated from the following phenomena: 1) dissolving; 2) surface activation; 3) enzymatic effects; 4) chemical reactions and 5) physical effects, which have been summarised in Table 2.2.

Table 2.2 A summary for different cleaning forces

Categories		**Interaction ways**
Dissolving		Soluble contaminants are dissolved in solvent and then steadily dispersed into cleaning agents.
Surface activation		Lowering the interfacial tension between surfactants and contaminations by wetting, permeating, emulsifying, scattering and solubilising.
Enzymatic effects		Specific organic contaminants can be decomposed via hydrolysis reaction accelerated by catalysis effect of the enzyme and disperse into cleaning agents.
Chemical reaction		Contaminant molecules are decomposed by chemical reactions between cleaning agents and contaminants/substrates and then diffuse into the cleaning agents.
Physical effects	Thermal effect	Accelerating the cleaning process by decomposing contaminant molecules or changing physical properties through the temperature variances
	Pressure	Cleaning force induced by the pressure oscillations (varying from vacuum to high pressures) in the cleaning agents
	Friction	By rinsing object surfaces using cleaning agents and creating shearing forces between contaminant layers
	Abrasive forces	Via mechanical interactions acting on contaminant surfaces, such as steel shot blasting
	Ultrasound effect	By the cavitation effect induced by ultrasound in the cleaning agents between substrate materials and contaminant substances
	Electrolytic forces	Removing the contaminants by the micro bubbles generated in the electrolysis between substrate and cleaning agents

2.2.4 Cleansing Agent

A cleansing agent provides an environment that contact to both the substrate materials and contaminant substances. In the cleaning process, it plays a significant role of generating the cleaning forces for stripping contaminants off substrates,

dissolving soluble compounds, preventing contaminant re-adsorption and removing contaminants from the substrate adjacent areas. The commonly used cleaning agents are categorised into four kinds, namely organic solvents, aqueous based cleaning fluids, chemical solvents and solid particles (Brooks et al., 2005). 1) An organic solvent is one of the most conventional cleaning agents in the cleaning of oil, grease and other materials. Contaminants that are soaked in cleaning solvents are stripped off by dissolving forces and dispersion forces exerted on the interface between contaminants and substrates. 2) Aqueous based cleaning fluid is the cleaning agent capable of removing contaminants with complex compositions such as mixtures of organic liquid and inorganic salts. It mainly comprises surfactant, detergent, additive agent, etc. and exerts decontamination forces on contaminants by the effect of adsorption, wetting, permeating, emulsifying, scattering and solubilising. The dishwashing cleaning liquid like FAIRY is a feasible example of the aqueous based cleaning fluids. 3) Chemical solvents are usually employed in cleaning stubborn and insoluble contaminants such as rust and saponified grease. The cleaning force in chemical solvents is usually from the chemical reactions between contaminants and substances in the solvents, which usually contains acid, alkali, oxidising or reducing agents, etc. 4) In addition to the liquid-based cleaning agents, solid particles are another typical cleaning agent. It is primarily used to clean rusts, paint coatings, etc. on the cleaning objects by the abrasive forces and impact forces generated by high-speed collisions. The material selection for solid particles is based on the stiffness of contaminant layers and the property of substrate materials.

Cleansing agents play an essential role in remanufacturing cleaning:

interactions between the agent and the substrate core directly determine the removal rate of contamination and the surface morphology subsequent to the process. Cleaning technologies summarised in this chapter demonstrates that numerous kinds of chemical substances are utilised as cleansing agents due to their good dissolving ability. They can be generally categorised into two kinds: solvents and aqueous detergents. Solvents remove contamination by dissolving the contaminants, thus minimising the material impact on the core. Commonly used solvents are typically organic substances, such as alcohols and ketones, or petroleum based, such as petrol and chlorinated organics (Niemczewski, 1999). The volatility of solvents determines that little or no residue can be observed on the cleaned object. Nevertheless, the side effects of solvents being vaporised into the atmosphere cannot be neglected. Taking chlorinated organics for instance, substances containing fluorine can have detrimental effects on the ozone layer (Haas, 1992). Furthermore, health problems including allergies and asthma have been noted by cleaners, due to complex exposure to the vaporised cleaning solvent (Wolkoff et al., 1998). Aqueous detergents, which can reduce cleaners' exposure to vaporised solvents, mainly utilise adsorption, wetting, emulsification, dispersion and solubilisation to achieve the removal of contamination. Yet the residue of surfactant in the aqueous detergent will adhere to the core surfaces, making subsequent treatment difficult. Subsequent treatments that use physical cleaning such as high-pressure water jets, abrasive blasts, etc. may induce unexpected damage to the core surfaces (Bartha et al., 1996, Wilson et al., 2014). All these drawbacks compel people to seek for alternative cleaning methods for remanufacturing so as to meet the specification of sustainable manufacturing.

2.3 Cleaning Technologies for Remanufacture

The selection of cleaning technologies and equipment in remanufacturing is based on the motivations and corresponding cleanliness requirement at each stage. Currently, there is not a cleaning technology specifically exploited for remanufacturing; further investigations and improvements in cleaning techniques and facilities are essential for the "greener" development of remanufacturing. Although very few ideas can be borrowed from manufacturing industry, the current cleaning technologies used by OEMs can still provide the reference and scientific base for exploring new methods for remanufacturing.

2.3.1 Water Cleaning

Water is the most fundamental and conventional cleaning agent in industrial cleaning. Water cleaning is very effective in removing aqueous based contaminants such as soluble inorganic salts and bulk contaminants of dust and particle depositions, greases and oils. It can be used in different scenarios such as in ordinary immersion cleaning and high-pressure water steam or water jet cleaning. A very satisfactory result can be attained using water spray system or high-pressure water jet in removing, for instance, mill scales from steels and paint layers from aircraft. Water can be also used with the addition of other techniques such as detergents and ultrasound, to enhance the cleaning efficiency and eventual cleanliness. Water can be found in almost every aspect of industrial cleaning; therefore, the environmental problems caused by the wastewater remain and can be high-cost to deal with. Since large amount of water would be consumed in this process, researchers have developed a series of additives into water, transforming

the cleaning agent into aqueous based solutions, to promote the cleaning efficiency and extend its feasibility in removing more contaminants.

Acid based: Mineral acids or organic acids are added into water, sometimes with the addition of detergents or chelating agents. Contaminants such as scales, rusts and metallic oxides can be corroded through chemical reactions and dissolved by the acid based aqueous solutions. Acidic cleansers can effectively remove rust and water scales from substrate materials. However, acidic substances in the solvent are corrosive not only to the substrate material but also to humans.

Alkaline based: In alkaline based wet cleaning process, pH values of the aqueous solvent usually range from 8 up to 14, by adding alkaline substances into the water. This type of solvents is usually used in cleaning contaminants from manufacturing process, such as cutting fluids, coolants and others can react with alkaline substances in the solutions (Bird, 1995). The solvent can be used in various forms of cleaning processes e.g. sprays, immersion cleaning or combined with other facilities like ultrasonic generators. Sometimes, other additives may be used to improve solvent performance and characteristics, including emulsifiers, surfactants and sequestering agents. Alkaline cleaning is very effective in some scenarios; however, the environmental issues of this method cannot be ignored. The first problem is the handling of waste cleaning agents. Although the process has been modified such as filtering contaminants and reusing solvent in a closed loop system, the contaminants would cause pollutions to filters, which is an inevitable problem for this type of systems.

Neutral based: A neutral based solvent can achieve the removal of

contaminant by changing the surface tension of solvents rather than its pH values, by adding chemistries such as γ-valerolactone (Häckl and Kunz, 2018). Cleaning using neutral aqueous solvent could be relatively milder than acidic and alkaline cleaning, which primarily depends on the chemical reactions between solvents and contaminants. Neutral solvents are more feasible in the use of spray cleaning or ultrasonic cleaning operations. Similar to the other two aqueous cleaning, waste water is the primary pollution source that requires extra treatment.

Aqueous cleaning is one of the most conventional cleaning methods. From the above analysis, however, the waste water generated in this process remains the primary problem to be solved, along with others such as material corrosion, application limitations and subsequent requirement for a drying process. In addition, regulations have been proposed for wastewater disposal and corresponding environmental protection. It is therefore concluded that alternative cleaning techniques are essential to replace water cleaning.

2.3.2 Organic Solvent Cleaning

Organic solvents are one of the most commonly used conventional technique in cleaning processes. By soaking cores in organic solvents or spraying solvents onto the contaminant surfaces, removable compounds in contaminants can be dissolved or react with the solvent molecules to realise the contaminants removal (Kikuchi et al., 2011). A series of organic substances has been used as the solvent in an organic cleaning process such as acetone, ethanol, glycol ethers, petroleum distillates and so on. Despite the satisfactory cleaning results of this cleaning technique, the environmental problems caused by the volatile organic compound

(VOC) (Rajaei et al., 2012) and the waste liquid should be taken into special consideration. Currently used organic solvents have been summarised and selectively listed as follows.

Acetones: Acetone is primarily used in precision cleaning and protective cleaning of coatings, and plastics. It is an extremely volatile liquid substance; therefore, it is very suitable for dry cleaning. However, it should be handled with special care because it is a VOC with extremely flammable properties. Usually, it is recommended to be mixed with isopropanol (Fingerle et al., 2015).

Alcohols: Alcohols are similar to acetone, also a typical kind of organic solvents for dry cleaning with relatively high volatility and flammability. They could dissolve most of soluble substances in the contamination in a short period of time, therefore used for removal of organic substances of small molecules. However, alcohols are not effective in dissolving non-polar materials and macro-molecule substances such as waxes and oils. Moreover, they should be treated with special care as a VOC, especially when methanol is used because of its toxicity to the human health.

Dibasic esters (DBE): Dibasic esters refer to the kind of esters that possess two ester functional units in their molecular structure, usually a mixture of methyl esters of dicarboxylic acid such as adipic and succinic acid. DBE is very effective in the removal of paint coatings (Evans, 2005) in pure esters or as a mixture with NMP (N-Methyl Pyrollidone). Although it is also a VOC, DBE has a relatively low vapour pressure, which indicates that it can be used as the base solvents to mix with other chemical substances for the modification of cleaning ability. A pure

DBE has been estimated with threshold limit values (TLV) of 1 ppm, which should ensure the safety of operators' health.

Similar solvents include organic materials such as ethyl lactate solutions, glycol ethers, NMP, petroleum distillates and terpenes, which are VOCs with high flammability, toxicity and other environmental problems.

2.3.3 Abrasive Cleaning

Abrasive cleaning is a typical blasting process which uses abrasive materials as the cleaning agents (Taylor, 1973), primarily to remove surface layers such as rust, scale, etc. This cleaning technology uses abrasive materials propelled by compressed air or high-pressure liquid to impinge onto the target cleaning objects. Conventional abrasive materials are usually metallic balls, sand, ceramic grits or other materials with a relatively high hardness and propelled by air or water to obtain adequate kinetic energy for stripping contaminant substances off substrates. Currently, more materials have been exploited as the abrasive particles such as CO_2 pellets (Uhlmann and Hollan, 2015), wheat starch (Djurovic et al., 1999) and sodium bicarbonate (Kurtz, 1994), which can introduce new mechanisms into the removal process. Abrasive cleaning has very satisfactory results in removal of heavy scale and paint coatings. Methods of applying abrasive materials can be classified into two types, i.e. dry and wet (CDC/NIOSH, 1976), based on the propellant materials. Although abrasive cleaning has good excellent effect, pollution induced by fine particles generated during the impinging process, suspending in the atmosphere can become a hazardous waste that affect the health for operators. Therefore, extra handling is usually required in this process. Moreover, the abrasive

cleaning always brings changes in the surface finish of substrate materials and dimensional changes in the structures of thin walls.

2.3.4 Spray Cleaning

In spray cleaning technology, target contaminants are removed by streams of diluted cleaning solutions which are accelerated by pumps and sprayed out through spraying nozzles. The mechanism of this technology is similar with the abrasive cleaning which has been outlined in 2.3.3, except that the abrasive materials are replaced by liquid materials. Based on the pressure differences, spray cleaning can be categorised into high-pressure and low-pressure sprays.

High-pressure spray: It can be used in almost all type of cleaning scenarios, from precision cleaning for as micro as structures such as disk drive parts to the cleaning of components from automobile. Usually, the high pressure in spray cleaning refers to a propelling pressure over 34 MPa, which is the read from pumps rather than actual pressure on the cleaned surfaces. Water is the most used liquid for spray cleaning; however, when being confronted with contaminants that are difficult to remove by pure water sprays, chemical additives can be mixed into cleaning sprays to attain satisfactory cleaning results through chemical reactions between additives and contamination compounds. High-pressure cleaning is very efficient in removing contaminants from blind, tapped holes, especially in the removal of particulate contaminants of less than 3 microns. It is usually used in the scenario that high cleanliness is required such as high-precision machining finish, while not necessary in cleaning component of relatively lower cleanliness requirement such as the removal of machining chips.

Low-pressure spray: Low-pressure spray cleaning is a similar cleaning technology with high pressure spray. One distinction between the two methods is the propelling pressure driving the cleaning liquid. The low pressure refers to a pump pressure ranging from 14 to 20 MPa, which generates weaker cleaning force onto the contaminants than high pressure sprays. Therefore, low-pressure spray cleaning is not feasible for cleaning strongly adhered contaminations while rinsing contaminants that have been loosen by previous process such as ultrasonic and chemical treatment would be much more suitable.

Spray cleaning can be a complete manual or highly automated process, which is either independently used or combined with other cleaning operations. Spray cleaning usually consumes large amount of water, which becomes the main pollution that should be treat in the post treatment process. Although chemical additives can increase the cleaning efficiency, the chemical additives should be low foaming to reduce the foam generation during spraying process. The addition of flammable or combustible substances may turn the sprays into highly explosive materials that should be taken extreme care of during the cleaning. Moreover, the moist with additive compositions in the atmosphere may also affect the health of operators; therefore, spray cleaning is still with some environment issues that are not qualified as a “green” cleaning technology.

2.3.5 Brushing

Brushing is a typical mechanical cleaning method that removes contaminants from substrate materials by mechanical abrasion between the brush and substrates. It is very effective in removing “dry” contaminants such as scales, rust, paint and

particle depositions, but has low efficiency in removing fluid contaminants. The violent abrasions between brush and substrate may lead to the loss of base materials during cleaning process; therefore, it has been used at the highest cleanliness level for semiconductor cleaning (Amsden et al., 1998). The brush is usually made of wires or of synthetic materials which are impregnated with abrasive particles. In the cleaning process, brush materials wipe off contaminant particles from base materials and usually with the loss of substrate materials. The operation conditions for brushing could also be various, from highly automated to totally manual cleaning. However, its application to has been limited by the base material loss during cleaning process.

2.3.6 Heat Cleaning

Heat cleaning, also known as thermal decomposition (THD), refers to the cleaning process that decomposes contaminants into smaller molecules to attain the required cleanliness (Gooch, 2011). It is a feasible method in cleaning oil depositions, coatings, mill scales and other substances that can be decomposed at high temperatures. Heat cleaning does not introduce additional solvents or cleansers into the cleaning system; therefore, it has high cleaning efficiency. However, high temperatures may lead to damages to some substrate materials which are thermal sensitive, for example unnecessary annealing. Consequently, heat cleaning is not a feasible approach for substrates with low melting points and thermally sensitive materials. Even though heat cleaning is with great efficiency and has been broadly used in industrial cleaning, its flaws and environment issues remains to be solved currently. During the heat cleaning process, large amount of exhausted gas is emitted into the atmosphere, which usually comprises acidic gases

such as SO_2 and NO_x. Moreover, heat cleaning requires large amounts of energy, which are primarily obtained from the combustions of coals or diesel. Endeavours are still required in exploiting "greener" and cleaner energy resources to reduce the pollution to environment and human health.

2.3.7 CO_2 Cleaning

With the arising concerns about global warming and other environmental issues occurring all over the world, researchers have been trying new techniques which can reduce the emission of greenhouse gases during the process (Baatz, 2014). Although these CO_2 gases will be eventually emitted to the atmosphere, the processes per se generate no additional CO_2 to the environment because CO_2 gases are primarily derived from other chemical process. Currently, a series of techniques using CO_2 as the cleaning agent has been invented for the cleaning industry. Two related methods are summarised in this section.

Dry ice cleaning: Dry ice cleaning should be de facto categorised into blasting type of decontamination process. CO_2 can be made into different sizes of dry ice particles by a proprietary facility. They are propelled by compressed air and impinge on contaminant layers in cleaning operations, where the speed of CO_2 ices can be regulated by adjusting the propelling pressure and pellet sizes (Spur et al., 1999). The dry ice blasting has an advantage that the solid CO_2 sublimates and vaporises after contact with contaminant materials, leaving only contamination to dispose of. In addition, the sublimation process requires large amount of heat; therefore, liquid contaminants could be locally frozen into contaminant scales in the blasting process. It is an very effective process in removing compact coatings,

sealants, greases and even liquid oils (Archibald, 1993) from metallic substrates like aircraft materials. However, this process is not designed for heavily contaminated parts. It is therefore not feasible for remanufacturing because cores are usually with large amount of pollutants on their surfaces.

CO_2 snow cleaning: Carbon dioxide snow cleaning is another contamination removal technology using CO_2. This process uses the flake-like dry ices which are directly transformed from gas phases CO_2 (Sherman et al., 1994). It is very effective in the removal of particles of small size (as small as 0.03 micron) and organic compounds such as hydrocarbon and grease residues from silicon wafers (Sherman and Whitlock, 1990). The removal mechanism of this process is still controversial as researchers had proposed different theories to describe the contamination removal process. Some research indicated that the removal involves a comprehensive effect of gases in high velocity and momentum transfer, where contaminant particles are removed by collisions with CO_2 "snowflakes" (Sherman and Adams, 1996). However, other study shows a contrary mechanism, which argues that the kinetic energy in this process has little effect on contaminant removal; the phase transaction from solid to gas phase provides the removal forces for the cleaning process. CO_2 snow is effective in cleaning particle contaminants; it is therefore suitable for the cleaning process which requires relatively high cleanliness levels.

2.3.8 Acoustic Cleaning

Acoustic cleanings refer to the process where the cleaning operations derive energy from soundwaves and transmit these severe oscillations through cleaning

agents to generate cleaning forces. Based on the frequency differences of soundwaves, acoustic cleaning can be categorised into ultrasonic cleaning (20-40 kHz) and megasonic cleaning (700-1000 kHz).

Ultrasonic cleaning: This method has been widely used in many scenarios requiring cleaning operations, with very high cleaning efficiency for cleaning many types of contaminants. A basic ultrasonic cleaning device includes a cleaning vessel, one or more transducers, ultrasonic generators and cleaning agents that are usually in liquid phase (Bland, 1961). In the cleaning facility, each transducer is coupled with one generator that can be operated in the range of 20-40 kHz and the number of transducers determines the overall energy output of the apparatus. Typically, these transducers are positioned under the cleaning vessel, transmitting high-frequency vibrations to the liquids in the vessel. The high frequency pressure agitates cleaning liquids and generates bubbles, forming and collapsing rapidly under the cavitation effects. The pressure within the cavitation bubbles can reach as high as 200 kN with the temperature of nearly 6000 K. Therefore, very strong cleaning forces can be generated in the ultrasonic environment for the removal of contaminants adhering to the substrate materials.

Although ultrasonic cleaning technology has been widely used for workpieces in different shapes, sizes and materials and has achieved excellent cleaning results, the limitations of this technology are also apparent applications. For instance, cleaning liquids sometimes cannot penetrate blind holes in MEMS (Micro-Electro-Mechanical System) structures and generate air bubbles there due to surface tension; consequently, the ultrasonic waves are not able to generate cavitation bubbles in these holes. Cleaning effects are therefore significantly reduced.

Moreover, the high intensity vibrations from ultrasonic devices are damaging not only to the contaminants, but also the substrate materials, especially those MEMS devices. Study has shown that the substrate erosions can be found in almost any materials, such as glass and aluminium alloys (Krefting et al., 2004). The chemical solutions used in this technology is another problematic aspect that requires additional treatment after the parts are cleaned. Therefore, the further study exploring environmentally friendly chemical solutions in ultrasonic cleaning is an interesting area of research for the academic community.

Megasonic cleaning: Megasonic cleaning is another acoustic cleaning technique. Comparing with ultrasonic cleaning, it is a milder method, which uses sound waves at higher frequency, ranging from 700-1000 kHz. Megasonic cleaning is effective in removing submicron particles from silicon wafers in aqueous baths (Busnaina et al., 1995) without wafer damage, since cavitation effects in a megasonic environment is much less damaging than those in the ultrasonic cleaning bath. In a same solution, the cavitation effect can be found throughout the liquid, while the acoustic waves in a megasonic cleaning apparatus are only observed in the adjacent regions surrounding the transducer surfaces. Therefore, megasonic cleaning is a line of sight cleaning technology and only the side that faces the transducers can be effective cleaned.

2.3.9 Laser Ablation

Laser ablation is usually used for removing materials from a solid surface by irradiating target substances with laser beams with short pulse of high peak power. In this process, target materials absorb the energy of the laser beam, evaporate or

sublimate at a relatively low input power, or even transform into plasma at higher laser flux. Therefore, this technique can be used for removing contaminants on a solid surface, especially for the particulate cleaning from silicon wafers (Tam et al., 1992). In the cleaning of micro structures using laser produced steam, a thin liquid film covering the contaminants can enhance the removal efficiency of particle contaminants, which is called “steam laser cleaning” (Tam et al., 1998). Here, the thin layer of transfer media evaporates after absorbing energy of laser beams and carries off particulate contaminants from the substrate materials. Currently, laser ablation has been used in cleaning of such as particulate contaminants on silicon wafers, paint coatings on aircraft surfaces and thermal barrier coatings on turbine components. This operation can work on either completely or partially assembled components. Very little waste is generated since most of the contaminants have been evaporated during the laser ablation operation. However, laser ablation has very low cleaning efficiency when confronting complex structures and the high energy consumptions remain to be solved in the future studies.

2.3.10 Supercritical Fluid Cleaning

This technology uses a supercritical fluid (SCF) as the agent to achieve contaminant removals. A supercritical fluid is a substance with temperature and pressure both above its critical point, where the distinct liquid and gas phases no longer exist (Parris, 2010). In the supercritical phase, a fluid has unique characteristics such as the diffusivity close to a gas and the density similar with a liquid, endowing the fluid excellent solvency for many contaminants. Currently, water and CO_2 are the most commonly used fluids for supercritical process. In SCF

cleaning by use of CO_2, the contaminated parts are placed in a high-pressure chamber being operated at temperature over 31 °C and pressure above 7.38 MPa. The effect for cleaning parts with complex shapes and structures is quite good because SCF can penetrate the parts of due to its high diffusivity.

The supercritical cleaning process exhibits high cleaning efficiency on fluid contaminants, especially when CO_2 is used as the cleaning agents, because the liquid compounds usually have higher solubility than that of a solid material. Currently, SC-CO_2 cleaning is primarily used for cleaning textile products (Aslanidou et al., 2016), machining oils from metal lines (Ramachandrarao, 2006). In addition, small pressure changes in the adjacent area around the critical point can lead to significant changes of the fluid properties, so the cleaning process can be optimised by regulating the operating parameters. Research has also shown that SCF cleaning is effective in removing particles on microstructures such as for the rollers of printing industry (Della Porta et al., 2006) and in micro-electronics processing (Weibel and Ober, 2003). Although the initial investment for a SCF apparatus may be high, the cost for the on-going operations would be relatively low.

2.4 Trend for Cleaning Technology

As one of the vital processes for the mechanical equipment remanufacturing, cleaning operations should be an economical process that follows principles of high efficiency, energy saving and low pollutant emissions to the atmosphere including waste gases, liquids and solids. The present agents used in the cleaning industry usually comprise of organic compounds including chlorofluorocarbon

(CFC), ozone depleting substances (ODS), etc., many of which have been phased out due to environmental regulations like the Montreal Protocol and continued regulatory pressures. Thereby, the study of alternative solvents with environmentally friendly characteristics becomes a development activity for remanufacturing cleaning technology. Some principles should be followed when selecting feasible alternatives as cleaning solvent. The cleaning agent candidate should achieve excellent cleaning results and not be toxic or detrimental to the environment and operators. Therefore, conventional organic agents such as CFC-113, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) that have been eliminated from use are not feasible for engine component cleaning in remanufacturing operations. In contrast, cleaning methods such as brushing, acoustic cleaning and heat cleaning are intuitively "greener" to the environment considering their little emissions to the atmosphere.

Moreover, there has been increasing requirement of efficient and economical cleaning system with the ability of dealing with large-scale equipment for the remanufacturing industry, especially in the circumstance of increasingly higher remanufacturing demands. The requirements are driving manufacturers to explore and apply equipment with high automation characteristics, for all the process in remanufacturing rather than only in cleaning. Therefore, the research and development is focusing on the semi or full automatic cleaning production lines for the cleaning operations. Another trend in the research of cleaning technology is surrounding the exploitation of compound cleaning technology with a higher automation level, less detrimental emissions and lower costs.

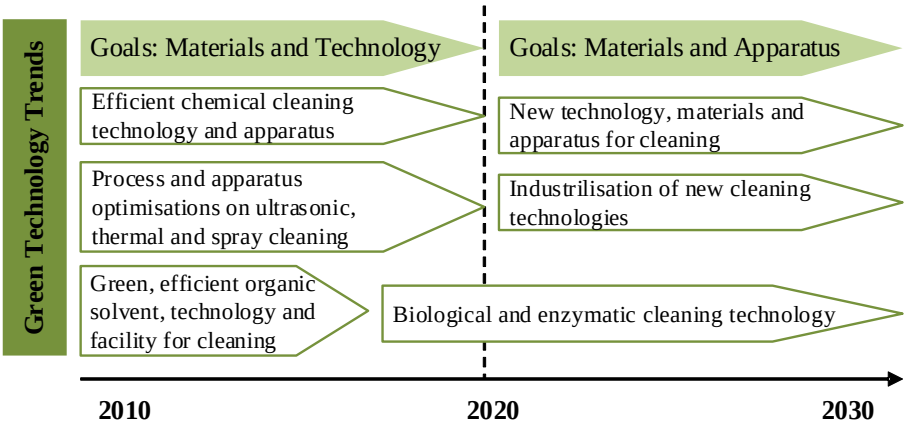

Fig. 2.1 The trend of the remanufacturing cleaning

The exploitation of newly invented "greener" technology usually requires high capital investment at its initial stages. To find an optimal balance between the economic and environmental requirements therefore becomes a significant issue for remanufacturing cleaning so that green manufacturing can be achieved in a relatively economic way. Fig. 2.1 gives the development tendency for remanufacturing cleaning technologies. Recently, a new idea for cleaning using a biological approach such as enzyme has been proposed by biological engineers for the cleaning industry. However, the state-of-the-art research only reports the studies of biological and medical related cleaning operations using enzymes as the cleaning agents (Khan et al., 2014). Besides the technology revolution requirement for cleaning operation in the remanufacturing industry, other technological supports also need improvement and innovation. This includes the classification of contaminant categories prior to cleaning process, fast cleanliness evaluation technology after cleaning, etc..

2.5 Principles in Selecting Cleaning Technology

When selecting one cleaning technology for a specific cleaning process in remanufacturing, several factors should be taken into consideration, which may include the cleanliness requirement, damages to the substrate materials, cleaning efficiency and the impacts to the environment and operating spaces. General principles for technology selection and optimisations are:

1) Recognising the objectives of specific cleaning process and the technical cleanliness requirements. The cleanliness requirements are distinct at different stages of remanufacturing such as disassembly, inspection or remediation, as described in Table 2.3.

2) Identifying contaminant categories on the cores and the adhesive mechanism, recognising cores' material, geometric dimensions and corresponding cleanliness requirement and then choose a feasible cleaning technology based on the analysis. In the meantime, comprehensively evaluate the cleaning efficiency, cost and probable damages to substrate materials.

3) Evaluate the energy consumption, waste emissions and environmental impact of the selected technology. Guarantee the cleaning process would be environmentally friendly and benign.

Table 2.3 Cleaning processes at different stages for automobile remanufacturing operations

Cleaning process	Contaminant categories	Goals	Cleanliness requirement
External cleaning prior to disassembly	Contaminants such as dust, silt, rust and scales on the external of equipment	For the convenience of product disassembly and preventing secondary pollution to the workshop	No dust falling off the surface
Cleaning for disassembled parts prior to inspection	Greases, rust, carbon and scale deposit, etc that adheres to surfaces of disassembled parts	Convenient for defect inspection on cores and remanufacturability evaluation	Substrate materials visible
Prior to remediation	Residues from inspection processes	To guarantee the precisions and quality of the remanufactured products	Depends on the precision requirement
Prior to assemble	Machining residues such as cutting fluids, greases, abrasive materials on the remanufactured products	To ensure the assembly accuracy of the remanufacturing products	Very clean
Prior to painting and packaging	Greases and other contaminants adhering to the surfaces during assembly	To guarantee the integrity of protection coatings and product appearances	Very clean

2.6 Summary

Cleaning processes are of great significance and demand in remanufacturing, which significantly affects the quality of remanufactured products and determines the overall environmental performances of the remanufacturing technology. It generally includes five different cleaning processes required for the remanufacturing production between different stages, i.e. cleaning prior to overall disassembly, inspection, remediation, reassembly and packaging. The cleaning operations for remanufacturing and original manufacturing faces different contaminant types, pollution degrees, operating procedures, etc. This chapter concluded the commonly used cleaning methods used in recent industrial

utilisations. The review on cleaning methods indicates that different cleaning technologies have different scopes of applications. Cleaning operations are generally categorised into wet and dry cleaning, which are either environmentally unfriendly or have high cost in the capital investment. Wet cleaning is thought to be problematic from an environmental perspective since it involves the utilisation of more or less hazardous solvents and detergents (Sivakumar et al., 2009).

Considering that traditional organic solvents mostly have negative impacts on the atmosphere, there is an increasing demand in environmentally friendly cleansing agent for remanufacturing. A promising cleaning technology should use the agent that is easily accessible and environmentally friendly or at least benign and clean to a relatively high efficiency. Contaminants on diesel engines are usually organic substances, in either liquid or solid forms. According to the summary of currently used cleaning technologies, carbon dioxide is a promising cleaning agent because it is a by-product of many processes and is thus readily available. However, the CO_2 pellet and CO_2 snow cleaning both use CO_2 in a relatively open circumstance, which would directly emit to the air, bringing additional pressures to the environment. In comparison, supercritical CO_2 (SC-CO_2) is always kept in a close loop within the facility and very little emissions are discharged to the environment. SC-CO_2 per se also has some extraordinary properties that allows the cleaning of parts with micro or complex structures such as silicon wafers. Therefore, the supercritical carbon dioxide is selected as the agent for developing a “greener” cleaning technology for remanufacturing. Properties of this fluid are discussed in Chapter 3.

Chapter 3

Supercritical Fluids

Supercritical fluids are gaining ground as promising environmentally benign solvent. Following on from ideas in Chapter 2 that supercritical fluid can be a promising cleaning solvent for remanufacturing cleaning process, this chapter introduces some fundamental knowledge surrounding supercritical fluids and its conventional applications, especially in the area closely related with material removal studies.

3.1 Introduction

The presence of a critical point of a pure substance was first discovered by Baron Charles Cagniard de la Tour in 1822 (Berche et al., 2009, Cagniard de La Tour, 1822) and Thomas Andrews named this phenomenon as supercritical (Andrews, 1869) in 1869. Since then, researchers have been attracted by the peculiar characteristics of supercritical fluids. A supercritical phase substance refers to the situation that its temperature and pressure are both above the critical values (Hedrick et al., 1992), i.e. the critical temperature (T_C) and pressure (P_C). The precise definition should be supplemented with "but below the pressure in the solidification line", which is usually omitted because the pressure required for solidification at this temperature is extremely high.

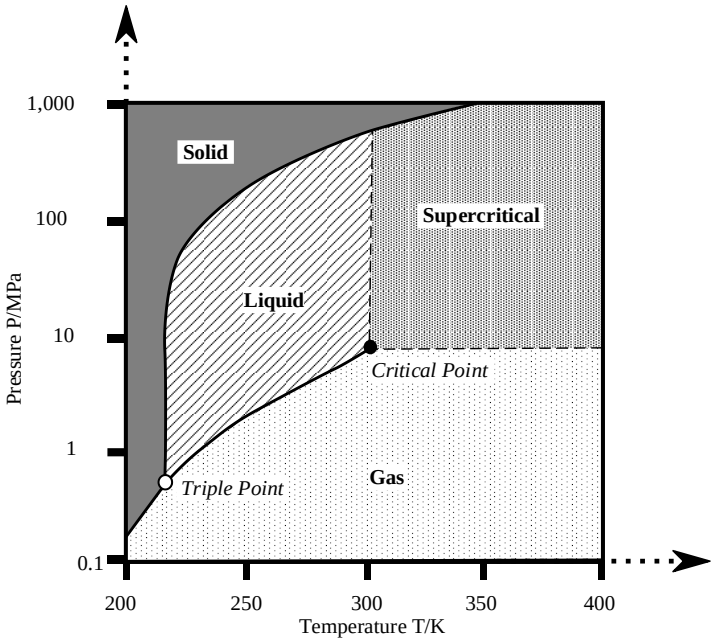

Fig. 3.1 Temperature-pressure phase diagram of carbon dioxide

It can be more easily understood with the assist of the CO_2 phase diagram, as illustrated in Fig. 3.1 The diagram illustrates the areas where the CO_2 is in the gas, solid, liquid or supercritical status. The curve between the triple point and the critical point, known as the boiling curve, are the parameters under which coexists both gas and liquid phase CO_2 in equilibrium. Moving upwards along the boiling line, liquid compositions tend to be sparse due to thermal expansions while gases becomes denser with the increasing pressure. When CO_2 temperature increases to T_C, CO_2 molecules could no longer liquefy even if the pressure is adequately high. Hence, the density of liquid and gas CO_2 become the same and the boundary of gas and liquid vanishes. In this condition, the fluid becomes a homogeneous supercritical phase, where the distinct gas or liquid do not exist. It has some properties of both gases and liquids such as liquid-like density and gas-like diffusivity; therefore, a SCF has some behaviours that neither of the two phases

possesses. In addition, the physiochemical properties of a pure SCF varies severely near its critical point; it is thus possible to control and regulate the dissolving ability of one SCF by tuning the operating parameters.

3.2 Supercritical Fluid Properties

This section introduces some properties of different supercritical fluids, which are substances with small molecular weights and simple molecular structures, among which carbon dioxide is a promising candidate.

3.2.1 Candidates for SCFs

Table 3.1 gives the information of some frequently used solvents in chemical industry, based on which the comparison of critical temperatures and pressures are demonstrated in Fig. 3.2. Currently, the SCFs have been widely used for industrial practices in a large scale (as high as 2000 litre vessels) while for cleaning operations remain in a small scale. The SC-CO_2 is still most popular option for a supercritical utilisation because of the inert properties in comparison with other solvents. For instance, the organic solvents in small molecular mass such as alkanes and olefins are extremely flammable, while the critical pressure for water is much higher than the conventional organic solvents.

Table 3.1 Critical properties of commonly used solvents (Reid et al., 1977)

Solvent	Molecular mass (g/mol)	Critical temperature (K)	Critical pressure (MPa)	Critical density ($kg \cdot m^{-3}$)
CO_2	44.01	304.1	7.375	0.466
CH_4	16.04	190.44	4.600	0.162
CH_3OH	32.04	512.54	8.092	0.272
C_2H_6	30.07	305.34	4.884	0.203
C_2H_4	28.05	282.24	5.041	0.215
C_2H_5OH	46.07	513.84	6.137	0.276
C_3H_8	44.09	369.74	4.250	0.217
H_2	2.01	38.35	1.665	0.0668
H_2O	18.02	647.10	22.06	0.322
H_2S	34.08	373.14	8.937	0.273

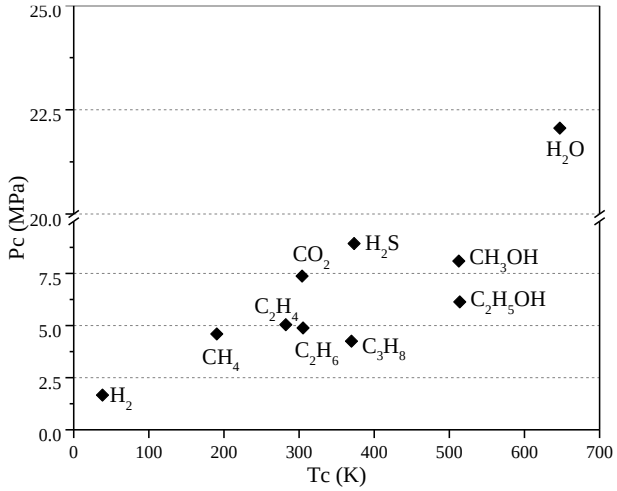

Fig. 3.2 Visualisation of the critical information in Table 3–1

3.2.2 Carbon Dioxide

CO_2 is a colourless gas that is naturally abundant in the atmosphere, with a simple, linear triatomic molecular system. It is a by-product of many processes and is thus easily available. It is inert, non-flammable, low in toxicity and naturally abundant (Beckman, 2004) and is therefore often promoted as a sustainable solvent

if kept in a closed cycle and not released to atmosphere. SC-CO_2 has been widely used in extraction (de Melo et al., 2014, Konar et al., 2014, Quach et al., 2014, Melo Silva et al., 2013), industrial dyeing (Banchero and Ferri, 2005, Hori and Kongdee, 2014, Long et al., 2014), purification (Chang et al., 2012, Huang et al., 2013, Kamarei et al., 2013), synthesis (Haldorai et al., 2012, Hong and Day, 2013, Middelkoop et al., 2014) and cleaning (Della Porta et al., 2006, Khanpour et al., 2014, Weibel and Ober, 2003). The use of CO_2 in SCF cleaning would be an innovative replacement of traditional cleansing agents, whilst the required technology has greatly developed, partly as a consequence of stringent laws restricting the use of VOCs. The properties of SC-CO_2, including relatively low viscosity, near zero surface tension, liquid-like high density and high diffusivity, allow it to promote mass transfer. Additionally, the operating conditions – the critical point of CO_2 (Tc = 31 °C, Pc = 7.38 MPa) – are easily attained and are relatively benign. Emissions of the process are a mixture of CO_2 and contaminants that can be separated easily by depressurisation; they are mostly non-flammable, non-corrosive and there is no hazardous waste. As a by-product in many industrial processes, SC-CO_2 utilisation does not generate extra CO_2 emissions to the atmosphere; therefore, its industrial utilisation is a promising innovation for reducing emissions of green-house gases. Finally, the relatively low cleaning temperature minimises any impact on the original surface properties and guarantees that the application of SC-CO_2 could preserve the thermal-sensitive properties of treated substances, such as in biochemical material synthesis and pharmaceutical applications.

Using SC-CO_2 as the cleaning agent to replace the organic solvents, one

benefit is the adjustable density, which, in return, has significantly affected the dissolution of contaminant compounds during cleaning. More importantly, the SCFs possess extraordinary characteristics such as higher diffusivity, lower viscosity and better transportation properties, making it a promising agent that could achieve the removal of contaminants while protecting the microstructures from destructions induced by the surface tension of liquid cleaning agents. However, the dissolving behaviours may be different in a supercritical environment than in a traditional gas or liquid solvent. Therefore, the necessity is apparent to gain insights into the dissolving process for parameter optimisations in the cleaning process.

3.2.3 Properties of a SCF

A SCF cleaning process primary depends on its high solubility compared with that of a gas. Among the parameters, density is the primary factor that influences the solubility in a SCF since the dissolution process relies on interactions between molecules of solutes and solvents. One crucial characteristic of a SCF is the inhomogeneity of molecular distributions (Nishikawa and Morita, 2000), resulting in significant density fluctuations in the local regions of a SCF (Tucker, 1999). When solutes are dissolved in supercritical solvents, the molecules would quickly cluster around solute molecules owing to the attractive solvent-solute interactions. This phenomenon is much more widely observed in supercritical fluids than in liquid solvents and is called “solvation”, “clustering” or “density augmentation” (Song et al., 2000).

This could be understood with the help of a schematic diagram of solute and

solvent molecules in different phases, as illustrated in Fig. 3.3. The left diagram depicts the binary system where molecules of the solid compounds dissolves in gas phase solvent. Comparing with the gas diagram, the density of liquid solutions (illustrated in the right diagram) is much higher, providing more frequent molecule interactions and therefore higher solvation. Unlike free molecules that distribute evenly in the gas and liquid phases, in a SCF, the solvent molecules are more likely to cluster around the solute molecule by forces of Columbic interactions, Lennard-Jones potentials, Van der Waals forces, etc. Research has reported that the deviation between average density and local value in the vicinity of solute molecules would be as high as 300% (Song et al., 2000). This characteristic significantly influenced the utilisation of SCFs in cleaning processes.

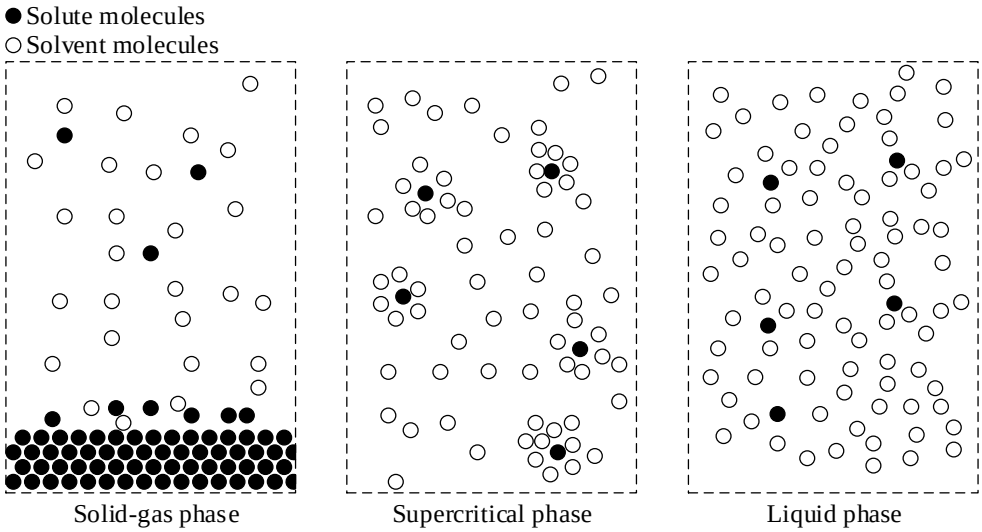

Fig. 3.3 Molecule distributions in different phases

Table 3.2 Transportation properties comparisons between different phases

Properties	Gas	SCF		Liquid
		T_C, p_C	~T_C, 4 p_C	
Density (g/cm^3)	(0.6~2)×10^{-3}	0.2~0.5	0.4~0.9	0.6~1.6
Dynamic viscosity (mPa·s)	0.01~0.03	0.01~0.03	0.03~0.09	0.2~3.0
Diffusion coefficient (cm^2/s)	0.1~0.4	0.7×10^{-3}	0.2×10^{-3}	(0.2~2)×10^{-5}

Table 3.2 gives a comparison of some physical properties of gases, liquids and SCFs in terms of density, dynamic viscosity and diffusion coefficient. It can be observed that the density of a SCF is similar with that of a liquid, which is about 100 times greater than that of a gas. The solubility of one substance in the SCF will be therefore much greater than in its gas solutions because interactions between molecules are stronger and more frequent. Besides the liquid-like fluid density, a SCF possesses a viscosity much similar with that of a gas, determining that the SCF could diffuse into the micro structures of many products like a gas. Greater amount of SCF molecules can drag more target compounds from the microstructures and benefit material transportations in the overall process. The transportation properties of a SCF stand between gas and liquid. The diffusion coefficient of a SCF ranges from 0.7×10^{-3} to 0.2×10^{-3} cm^2/s, approximately 100 times greater than the liquid. Theoretically, a SCF should has better performance in the mass transportation process than both gases and liquids. The extraordinary properties make SCFs a suitable type of solvents for material removed processes such as extraction and cleaning.

3.3 Material Removals Using SC-CO_2

With high diffusivity, low surface tension and viscosity, it is usually considered that material removal process using SCFs do not experience the

limitations of conventional liquid extract. Research has been conducted from many aspects surrounding material removal, including parameter investigations (Della Porta et al., 2006), co-solvent utilisation (van Roosmalen et al., 2003b), modelling and process optimisation (Wei and Yang, 2015), etc..

The cleaning operation using SC-CO_2 has a similar mechanism as the extraction process: both are closely related to material removal. Currently, the extractions using SC-CO_2 has been very well developed in removing or extracting specific kinds of organic compounds from plants, such as the decaffeinating of coffee beans (Peker et al., 1992) and extracting lycopene from tomato skins (Yang et al., 1995) . Removal rates, or extraction yields, are apparently the ultimate goal for this process. The processing conditions for different substances vary in SC-CO_2 processing since each substance has distinct solubilities in SC-CO_2 fluid. Consequently, the primary issue dealing with a new material in SC-CO_2 extraction is to obtain the optimal processing conditions. Basic parameters for the processing include temperature, pressure, flow rate, time, co-solvent using and the particle sizes of the processed materials. However, studies from different materials drew different conclusions on the significant parameters that affect the cleaning process. The investigation on extracting lavender essential oils demonstrates pressure and extracting time had a linear effect on the yields (Danh et al., 2012) while the extraction of piperine from black peppers (May Lin et al., 2013) shows that pressure, particle size and their interaction terms have the major influence on the extraction yields. Therefore, when using the SCF to remove one specific substance, the very first step is the determination of significant parameters and their effects on the final yields.

To explore the impacts on the production yield from different parameters, a series of methods have been used for the experiment design process, among which the DoE (design of experiment) technique is one of the most commonly used. For instance, a small face central composite design can be used for parameter optimisation for extraction. The response surface methodology (Özkal et al., 2005, Chang et al., 2012) has been widely used in determining the effects of different parameters mentioned above and fitted second-order polynomial models are usually used to describe their independent and interaction effects on the removal/extraction rate (Rai et al., 2015).

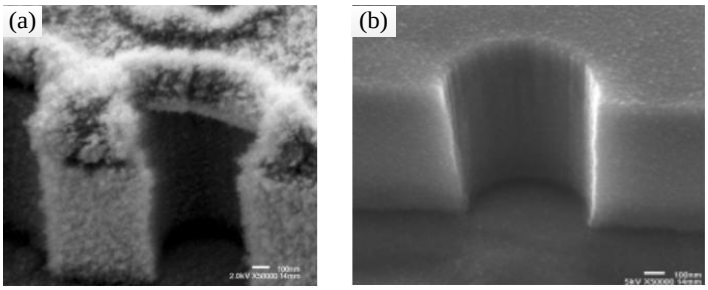

Fig. 3.4 The stripping process of the wafer photoresist in the SC-CO_2 atmosphere (King et al., 2003)

The SC-CO_2 has been broadly used in extracting specific material, and related technologies are also well-developed. Similarly, reports are found in cleaning by use of a supercritical fluid, especially in the field of the electronic component manufacturing industry. SC-CO_2 cleaning could maximally preserve the original structures of components, such as the non-destructive cleaning of probes for atomic force microscopy (Timashev et al., 2014) and the engraved rollers with microscopic cells (Della Porta et al., 2006). Fig. 3.4 is the comparison of a silicon wafer, prior to and after SC-CO_2 treatment in removing photoresists (King et al.,

2003). A cleaning result was obtained without damaging the structure of the silicon wafers.

In the production of metallic contacts, they could probably be stained with lubricating oil, which significantly affects the performance of these components. Researchers has proposed using SC-CO_2 as a greener solution to replace conventional agents (Viguera et al., 2013), and the study focused on the impacts of operating parameters on the cleaning efficiency. However, results demonstrated that it was impossible to totally remove the contaminants on the components within the range of parameters. Despite this fact, using the tuneable properties of SCFs, the attempts of using this technology different cleaning and degreasing processes can be still found in many industry applications, such as the textile cleaning (Aslanidou et al., 2016), waste oil cleaning (Fu and Matthews, 1999) and drilling muds (Khanpour et al., 2014). These results have shown ideal degreasing performance of using SC-CO_2 as the solvent but the optimal conditions for processing were different in each study. Similar studies has also been conducted in removing natural fat from sheep skins (Marsal et al., 2000) and the degreasing rate could reach 94%; however, the presence of water in the sheep skins negatively influenced the productivity.

The solubility of non-polar organic substances in the SC-CO_2 fluid is very high, some of which are even on the same order of magnitude as liquid solvents. However, despite SC-CO_2 has excellent performance in extracting/removing designated substances from a given substance, the limitations of SC-CO_2 application are especially apparent when dealing with polarity compounds. In addition, the removal efficiency is also a significant factor affecting the process

performance. Researchers have proposed many modification approaches to increase efficiency of SC-CO_2 treatment process, including physical and chemical agitations. In extracting lycopene and β-carotene from tomatoes, ethanol and canola oil were studied as the co-solvents to promote the extraction efficiency with the co-solvents of different mass fraction additions (Saldaña et al., 2010). Among the co-solvent utilisations, ethanol is one of the most frequently added materials in the SCF system since it was relatively low toxicity and easily accessible, while other additives can be also seen from literatures including methanol, propanol, acetone, etc. (van Roosmalen et al., 2003b). Mechanical agitations are another promising means in improving the removing efficiency of SC-CO_2 process. Acoustic agitation is a potential efficient method in enhancing the material transportations in the supercritical atmosphere (Farouk and Hasan, 2015). Experiments verified that the use of acoustic waves significantly accelerates the extracting process, especially those being operated near the critical point, increasing both the extracting efficiency and the final yield. Ultrasound is also a promising approach in promoting the extraction yields. With the addition of ultrasounds into the system extracting oleanolic and ursolic acids from herbs, the time for reaching extraction equilibrium is significantly shortened (Wei and Yang, 2015). In removing contaminants from deep, micro holes on silicon structures, SC-CO_2 pulse pressure cleaning (PPC) is found to have great productivity (Ota and Tsutsumi, 2008). Besides the parameters mentioned above, the dimensional factors of the cleaning object had also been taken into consideration. This method is able to remove particles with a diameter of more than 50 nm from the holes, owing to the drastic changes of the fluid properties in the near critical regions.

3.4 Solubility in Supercritical Fluids

Cleaning with a SCF is considered a solvent-related kind of cleaning technique. The utilisation of SC-CO_2 in replacing traditional organic solvents provides many advantages to the cleaning process, which is partially contributed to by the unique properties of SCFs. The effectiveness of the replacement is primarily depended on the solubility of contaminants in the SCF. For this reason, contaminant solubility related to the cleaning process should be discussed.

Basically, solubility is defined as the maximum amount of one particular substance that can be dissolved in one-unit quantity of solvent. The dissolving process generally follows the rules of "like-dissolves-like", which means that solutes tend to dissolve in the solvent with a similar polarity. For example, inorganic salts are usually with very high polarity; therefore, they can more easily dissolve in a polar solvent such as water, while nonpolar or low-polarity substances tend to dissolve in a nonpolar solvent. In a cleaning process, the solubility of a substance in SCF is of great significance for its removal. Many researches have been focusing on study in determining the relationship between solubility of different substances and the SCFs' temperature and pressure, via either theoretical analysis or experiment measurements. Generally, the measurement of solubility is carried out on pure substances (Mchugh and Krukonis, 1986) while industrial practice always faces mixtures of many different materials. In this case, the results of study on pure compounds can only suggest that the mixtures can be removed. For industrial utilisation, it is still depended on experiments to determine the feasible operation parameters.

3.4.1 Contaminant Solubility

According to the IUPAC (International Union of Pure and Applied Chemistry) solubility is defined as the analytical composition of a saturated solution expressed as a proportion of a designated solute in a designated solvent (McNaught and Wilkinson, 1997). It can be expressed in forms of different units such as mole fractions, molarity, molality and mass solute per volume solvent, etc. The molarity concentration of one substance can be stated using Eq. (3.1)

$$C = \frac{x}{V} \tag{3.1}$$

where C denote the molarity concentration of the substance; x stands for the mole fractions of the given substance and V represents the molar volume of the pure fluid. A SCF's solvating ability is majorly depended on its density, polarity and volatility of solute substance. Temperature is a significant factor that affects characteristics mentioned above in the system. The relationship between the solubility of one compound (solid or semi solid) and fluid temperature is described by Eq. (3.2):

$$\ln x = \frac{\Delta H_f}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) \tag{3.2}$$

Here, the ΔH_f is the heat of fusion; T represents the fluid temperature and T_f is the melting temperature of the solute compounds. R denotes the gas constant with the value of 8.3145 J/(mol·K). The validation of Eq. (3.2) is based on the assumption that the heat capacity and volume remains constant at different temperatures.

In a process where the temperature of a supercritical fluid remains constant, the solubility of one substance initially decreases during pressurisation as the substance is diluted. While a rapid increment in the solubility can be observed if the pressure continues rising, which usually occurs around the critical pressure of the fluid due to the rapid increase in fluid density. The pressure where solubility starts to rise is called threshold pressure (King, 1989), i.e. solute begins to dissolve in a SCF. However, the solubility will decrease if the pressure continues to increase because the high pressure of the fluids squeezes solute out of the solution.

3.4.2 Cleaning Models

A model could describe the relationship between the dependent variable and the factors that could affect it. To establish a model for the cleaning process, one of the most significant factor that must be considered is the partition coefficient. It is the ratio depicted in Eq. (3.3) that material concentration in surface contaminants to the concentration in the solvent

$$P = \frac{[C_S]}{[C_f]} \tag{3.3}$$

where P is the partial coefficient, $[C_S]$ is the compound concentration in the surface contaminants and $[C_f]$ represents its concentration in the fluid. At the starting stage of cleaning, the contaminant concentration is high on the surface while gradually decreases because of mass transfer in across the interface of fluid and contaminants. The changes in $[C_S]$ and $[C_f]$ can be categorised into three types, whose trends are described in Fig. 3.5. The dot-dash line of C shows the situation that the partition coefficient remains constant during the cleaning process. However, it can be rarely

observed in the practical studies. Commonly observed cases are curves A and B. Curve B indicates that the solubility of contaminants materials is limited in the solvent; therefore, the partition coefficient here shows a decreasing trend during the cleaning process. The curve A, however, is the case that the concentration of contaminant in the solvent is determined by the amount on the surface rather than the solubility. Here, at the initial stage, the [C_S] drops very rapidly because the solubility is adequately high, resulting little impact on the material transportation. When the line reaches the asymptotic value, the adsorption of contaminant on the surface becomes the predominant factor in the dissolution. The cases analysed above are the situations that must be taken into account in the cleaning operation.

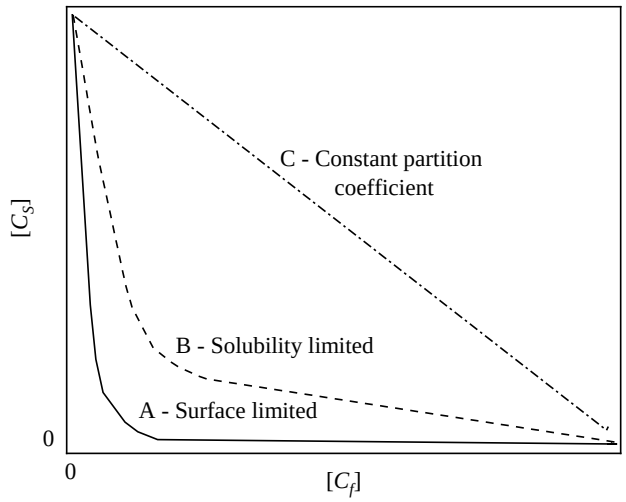

Fig. 3.5 Schematic diagram of partition coefficient in the form of concentration on surfaces and in fluids

Partitioning processes represent the concentration equilibrium of contaminant in different phases because it occurs in a back and forth way across the interface of the two phases. However, partitioning is not the only factor that should be considered in cleaning. The diffusion coefficient (D) describes the molecular

motion of contaminant substances from a higher concentration region to the lower region. A simplified model has been proposed to describe material transportation in a SCF (Laintz et al., 1998), as illustrated in Fig. 3.6. The subscript S denotes the surface, F is the SCF and L is the contaminant (either liquid or solid). The double subscripts in Fig. 3.6 mean the back and forth partitioning between two different phases. The soluble substances in the contaminant diffuse to the interface of contaminant and fluid in the boundary layer region, which can be considered as a static status. Those who are dissolved in the solvent then diffuse through the boundary layer into the SCF bulk flow. In the overall diffusion process, two diffusion coefficients are closely related, i.e. D_L within the contaminant and D_F in the boundary layer to the bulk flows. Due to the high fluidity and low viscosity of SCF, the actual cleaning (extracting) yields are more likely determined by the coefficient from surface to the contaminant, D_L, for the overall cleaning efficient, while extraction from contaminants into bulk flow is to be determined by the thickness of the boundary layer. A thick layer could prohibit the transferring to the bulk flow, therefore slowing down the dissolution process. To facilitate the material exchanges between contaminants and SCFs, the flow over the surface should be adequately high with a boundary layer as thin as possible.

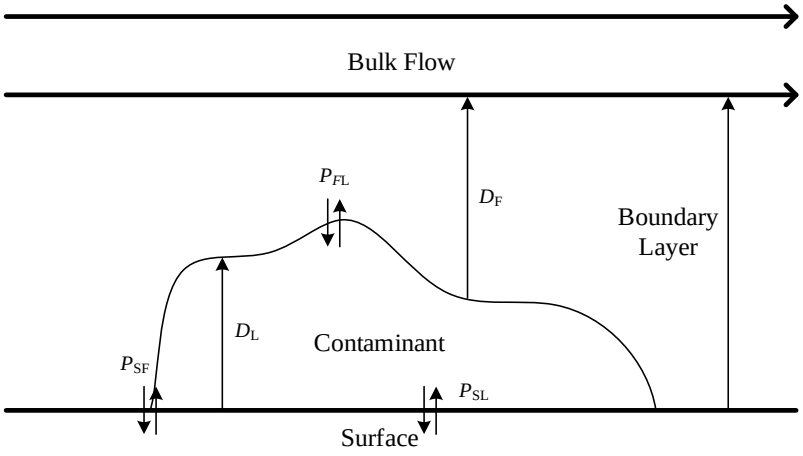

Fig. 3.6 A simplified model for mass transfer in the SCF cleaning (Laintz et al., 1998)

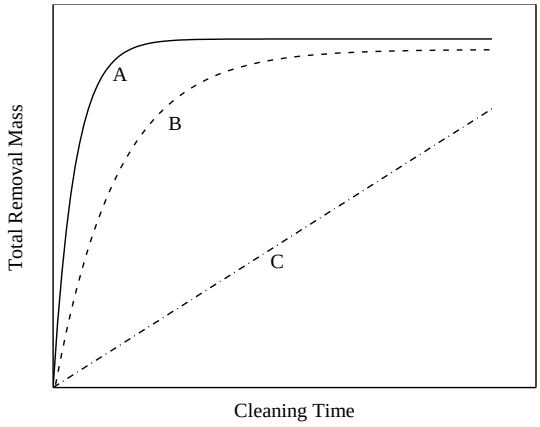

Fig. 3.7 A diagram for different situations of the removal mass and cleaning time

Fig. 3.7 shows three different cases in SCF cleaning. The line C in this figure depicts the situation that partition coefficient is a constant over the entire range of concentrations. It is usually observed in a static extraction/cleaning process or a limited solubility condition. Curve A shows the process with a very high cleaning efficiency, where the contaminants are very soluble in the SCF, maybe agitated by

the mechanical stirring to decrease the thickness of the boundary layer. Curve B stands between A and C, meaning the process is affected by both contaminant solubility and surface interactions.

3.5 Summary

This chapter introduced fundamental knowledge of supercritical fluids and related applications using SCFs. Currently, the applications of SCFs in industrial production are owing to its unique properties including high dissolving ability, low toxicity, low surface tension and no residues after separation. A SCF can mimic the properties of different solvents by regulating its pressure and temperature, therefore it can be used for replacing conventional solvents in chemical reactions. The adjustable density of a SCF near its critical point makes it an excellent solvent for dissolving and removing materials from a given substance and the separation of materials from the SCF can be also achieved effortlessly by simply depressurising the mixtures. Using these properties, SCFs, especially SC-CO_2, have been widely used in many industry applications including extractions, chemical synthesis and cleaning, where the optimal parameters for different processing are also different. Therefore, the first step is to investigate the optimal parameters when SC-CO_2 is used to handle a new type of substance.

In a cleaning process, the solubility of contaminants is a significant factor. Generally, the cleaning efficiency and removal rate of high solubility compounds are greater than that with a low solubility. Although the density of a SCF (also the solubility) increases with the pressure in the supercritical phase, a low processing pressure can reduce the overall equipment costs. In most cases, the impacts from

pressure are associated with the variations of pressure, as well. Therefore, in most conditions, the two parameters are optimised simultaneously to obtain the optimal contaminant solubility. The solubility of the contaminants can also be optimised by minimising the thickness of boundary layers, for example, using a turbulently flowing system or adding mechanical agitations into the system. The solubility can be enhanced by introducing a third compound such as a co-solvent into the system. The eventual cleaning result was influenced by many different variables associated with the process and these variables should be considered all together to achieve an optimal solubility, and eventually the cleaning efficiency.

Chapter 4

Experimental Facilities

Following on from the conclusion in Chapter 2 that SC-CO_2 would be a promising environmentally friendly cleaning solvent, Chapter 3 has introduced some fundamental knowledge of SCFs. This chapter illustrates the design of the test rig established for this thesis and related experiment facilities used in the research.

4.1 Supercritical Fluid Cleaning Test Rig

The piping and functional design was finished by our research group. Among all the work, the structural design of the cleaning vessel and separators were finished by me. Manufacturing work was accomplished by an SCF equipment manufacturer in Shenyang, China. The diagram in Fig. 4.1 illustrates the schematic SCF system and the assembled system in Fig. 4.2. Further demonstrations of the control panel and gauges can be referred to Appendix A. The design comprises cleaning vessel with volume of 1,000 ml, two 300 ml separators, gas storages and high-pressure pumps. Specifications for vital units in this test rig are summarised in Table 4.1.

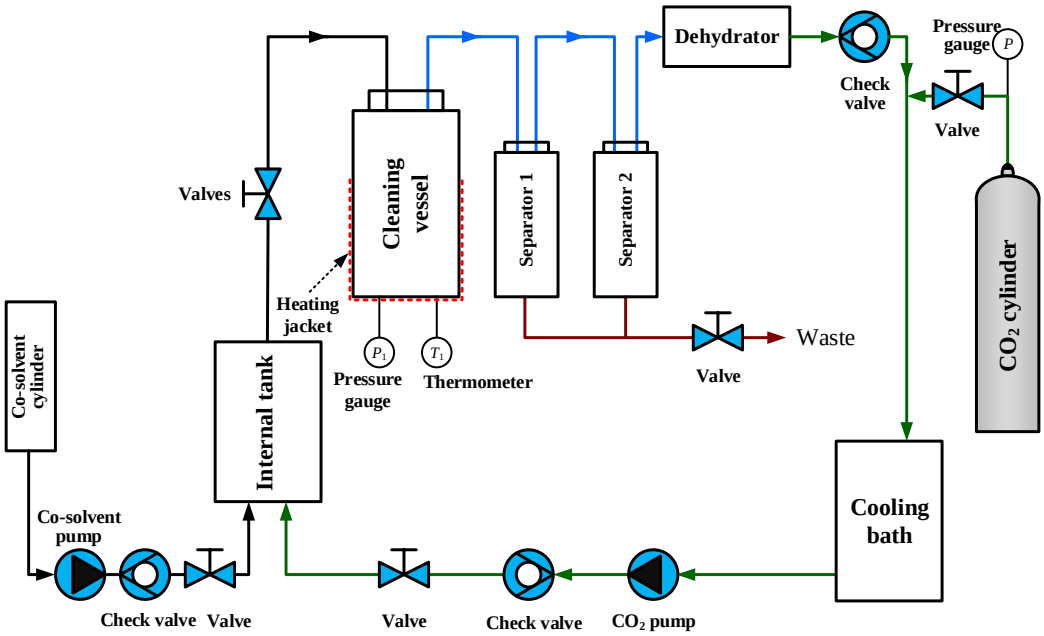

Fig. 4.1 Schematic of experimental test rig;

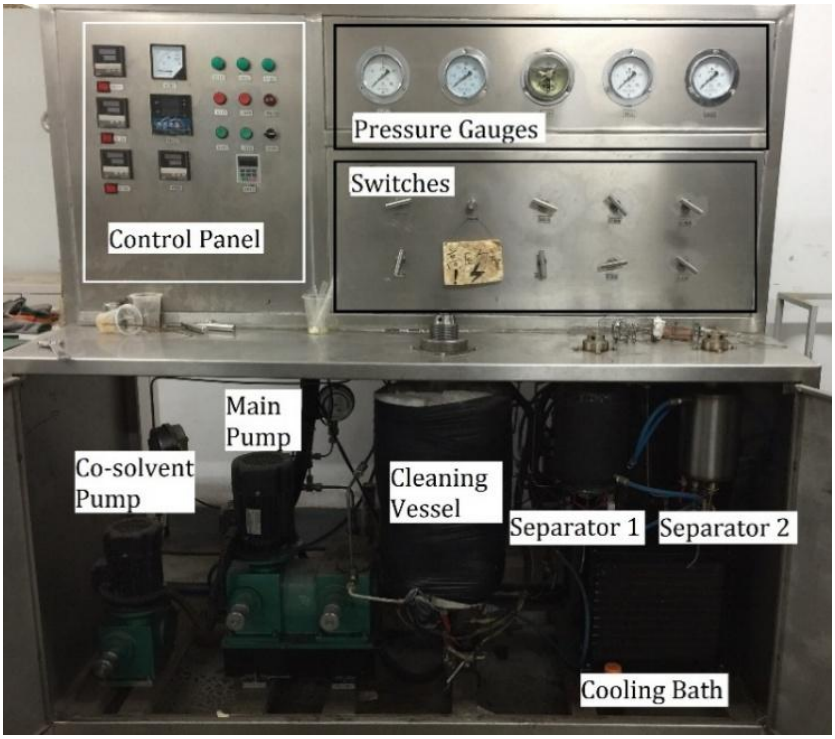

Fig. 4.2 Experimental test rig of supercritical fluid cleaning

Table 4.1 Experimental test rig specifications

Test Rig Detail	Specifications
Cleaning Vessel	Capacity 1,000 ml; Pressure 0.1–50 MPa; Temperature maximum to 300 °C
Separation Vessel – 1	Capacity 300 ml; Pressure 0.1–20 MPa; Temperature maximum to 75 °C
Separation Vessel – 2	Capacity 300 ml; Pressure 0.1–12 MPa; Temperature maximum to 75 °C
Internal Tank	Capacity 2,000 ml; Pressure up to 10 MPa; Pressure for safety pressure release valve 9.8 MPa
Co-solvent Vessel	Capacity 250 ml
CO_2 Pump	Plunger pump, 1–5 litre/h adjustable
Co-solvent Pump	Plunger pump, 0–0.5 litre/h adjustable

4.1.1 Internal Tank and Snubbers

The internal tank in this rig provided storage spaces for carbon dioxide, offering sufficient CO_2 supply when it is circulated within the system, transforming between gas, liquid and the supercritical phase.

Snubbers were installed between the internal tank and the cleaning vessel. This section supplied stable fluid streams into and out of the vessels, guaranteeing steady accumulation of solvents in the cleaning vessel and minimally reducing the fluid shocks induced by the plunger pumps. Through the addition of snubbers in the system, stable SCF streams in the cleaning vessel could offer relatively constant flow rates, reducing the apparatus error by fluid pulse. In addition, the snubbers also offered a more violent flowing environment in the internal tank. When co-solvents were introduced into the system, it could be ensured they had been well-mixed with carbon dioxide, prior to being charged into the cleaning vessel.

4.1.2 Cleaning Vessel

As all the dissociation processes of contaminations were achieved in the cleaning vessel, the design and manufacturing of the vessel should be of great significance. The drawing of the vessel assembly is illustrated in Fig. 4.3.

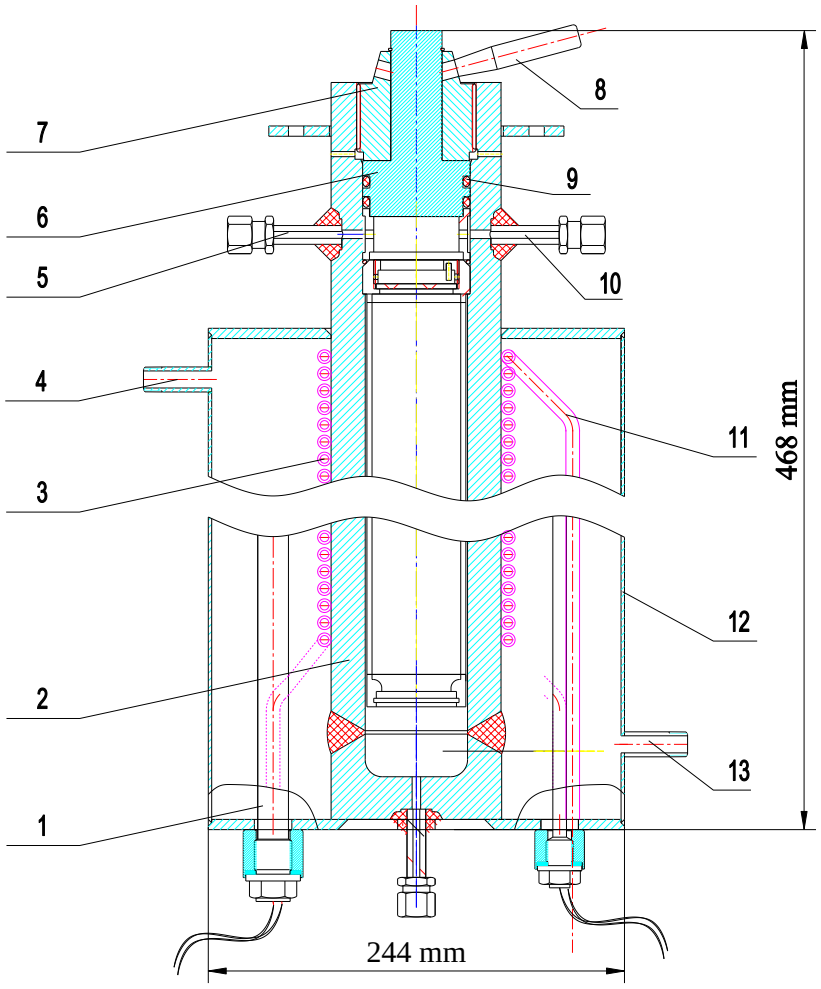

Fig. 4.3 Assembly drawing for cleaning vessel

1- Electrical heating tube, 2- Cylinder, 3- Heat exchanger, 4- Water inlet, 5- SCF inlet, 6- Internal seal, 7- External sealing cap, 8- Spanner, 9- Sealing rubber, 10- Heat exchanger, 11- SCF outlet, 12- Insulation housing, 13- Water outlet

The cleaning vessel primarily comprised a cylinder, internal and external sealing caps, sealing rubber and material baskets. The cylinder was made of 304 stainless-steel, forged with capacity of 1,000 ml by internal diameter of 60 mm and 360 mm length, offering a depth ratio of six. This design could guarantee adequate contacting duration of the SCF and test samples. Chromium and nickel in 304 steels impart the alloy good resistance against corrosions from working environment. Sealing of the cylinder was achieved through threads between cylinder end and the external sealing cap, along with sealing rubbers mounted between the internal sealing cap and cylinder body. When the sealing caps (6 and 7) were screwed into the cylinder, thread could bear the axial stress induced by pressure variations inside the cylinder and the atmosphere. Heating tubes surrounding the cleaning vessel offered isothermal conditions for tests, from heating water inside the insulation housing. The cleaning vessel could operate at pressure up to 50 MPa and temperature ranging from 30 °C to 200 °C. The precision of temperature and pressure of the cleaning system was ±2°C and ±0.2 MPa, respectively. Thermo-couples were placed on the external of the vessel and connected to a scanning thermometer to monitor the temperature of the micro-metering valve.

4.1.3 Separator Vessels

The SCF stream out of the cleaning vessel contained with extractable compounds that were removed from contaminations. To realise the circulation and recycle of CO_2 in the system, it is necessary to separate these substances from the fluid. Two separators after the cleaning vessel supplied the environment for complete removal of contaminating substances from SC-CO_2 stream. Their rated

working pressures were 20 and 12 MPa, respectively, with a same specification for working temperature of up to 75 °C. By regulating pressures and temperatures in the separation vessels, CO_2 fluid could transform from the supercritical phase into the gas phase, resulting in dramatically decrease in the solubility of the extractable contaminant compounds. Through two separators under different conditions, different compounds were precipitated and the purity of CO_2 fluid would be guaranteed for recycling. The structure of the separator vessels was similar with the design of the cleaning vessel, primarily comprising a cylinder, sealing caps and rubbers. At the bottom of the cylinder was an opening where extracts (contamination compounds) were discharged from the separator vessels. The cylinders were also made from 304-stainless steel, to resist corrosions from compounds of contamination.

4.1.4 Pumps and Dehydrator

The test rig was a closed-loop system. Prior to being charged into the cleaning vessel, CO_2 were initially cool down in the cooling batch, where the vapour would condense into water or ice. Those substances could cause serious pipe blocks and lead to equipment failures. Therefore, a dehydrator was installed between the gas inlet and the cooling bath to remove any water vapour in the CO_2 streams.

Pumps supplied impetus for the circulation of CO_2 in the test rig and controlled outflow rate of SCF in the cleaning vessel. As the only driving force for fluid flowing, the pumps should be simple-designed with reliable performances. Accordingly, a carbon dioxide plunger pump was used in the test rig, with the maximum outflow of 5 litres per hour. The outflow rate was proportional to the

rotor frequency which can be read from the digital metre on the control panel. The outflow rate Q could be calculated from (4.1)

$$Q = Q_{rtd} \frac{f}{f_{\max}} \tag{4.1}$$

where Q_{rtd} was the rated outflow of the CO_2 pump, f was the frequency read from the control panel and f_{max}=50 Hz was the maximum frequency the rotor could reach in this rig.

4.1.5 Experiment Procedures on SCF Rig

Procedures that the SCF cleaning operations followed were similar with respect to different contamination types and are elaborated with the assist of the schematic diagram in Fig. 4.1 in this section.

After the system were powered on, the cooling bath was initially started-up prior to all the other operations to decrease the cooling temperature to target value. This operation could ensure CO_2 could be liquified through the bath and pumped into the internal storage tank in the liquid phase, which would be easily charged into the cleaning vessel. In the test rig, the water circulation system and vessels **must** be pre-heated by the heating jackets prior pressurising for safety reasons that opposite operations could induce uncontrollable pressure increment in the vessel. Samples to be cleaned were placed in the cleaning vessel after the temperature reached the target value. Clean CO_2, which was usually stored in liquid form, was then charged into the vessel by the CO_2 pump, with or without the addition of co-solvent mixed in the internal storage tank. Static or dynamic cleaning operations

could be achieved by regulating the status of the valves before and after the cleaning vessel (both on – dynamic; both closed – static). Any sample in the cleaning vessel was then cleaned by being exposed to SC-CO_2 fluid. During the washing process, the CO_2 dissolved the contaminations and contaminated SC-CO2 was transferred from the cleaning chamber into the separator vessels where the fluid was decompressed and returned to a gaseous state for separation and recovery operations. The waste (concentrated contamination) was usually in the form of an oily or tar-like liquid residue, which were simply removed from the separator rank and recycled to reduce the solvent disposal costs, and the clean dry samples were removed from the vessel.

4.2 Liquid Blasting Test Rig

In this research, liquid blasting was used as the post-treatment operation to remove the residues after supercritical fluid cleaning. The single-particle shot test and liquid blasting cleaning was carried out on a cleaning equipment. It was modified from the liquid/dry shot peening machine (YT0-1308, Dotel, China) with an air compressor (FU22A, Fusheng, China). The assembly of the shot peening machine and the air compressor system is illustrated in Fig. 4.4. The facility was reconstructed based on the structure of a dry shot peeing machine. Compressed air, ejected from the compressor and through the inside of the nozzle, could bring out the peening grit from the supply pipe by the Bernoulli phenomenon, accelerate grit inside the nozzle to a certain speed and spray out of the nozzle onto test specimens.

(a) Shot Peening Facility (b) Air Compressor System

Fig. 4.4 Assembly of the liquid blasting system

The reconstruction was carried out on the control cabinet, the spray gun and the air supplying pipe. In Fig. 4.5 is the reconstructed control cabinet. Two switches were added, namely function selection button in black and the single particle button in green at the bottom, to achieve the wet blasting and single particle shooting functions in one piece of equipment. The Fig. 4.5 (b) illustrates the bottom view of the installation inside the spray gun, where the supplying pipes in Fig. 4.5 (c) were firmly fixed coaxially with the spray gun. Particles inside the hose are siphoned by the compressed air from the pipe next to the hose. The single-particle impact system was regulated at pressure ranging from 0.2 to 1.0 MPa, with ejection systems of 80 mm long and diameter of 6 mm to ensure the sufficient acceleration of grit particles. The global view of the reconstructed spray gun assembly is illustrated in Fig. 4.5 (d), with the specimen fixture that can adjust the

spray angle. The fixture was installed on the base through hinge and could achieve translations and rotations for experiment at different spraying angles

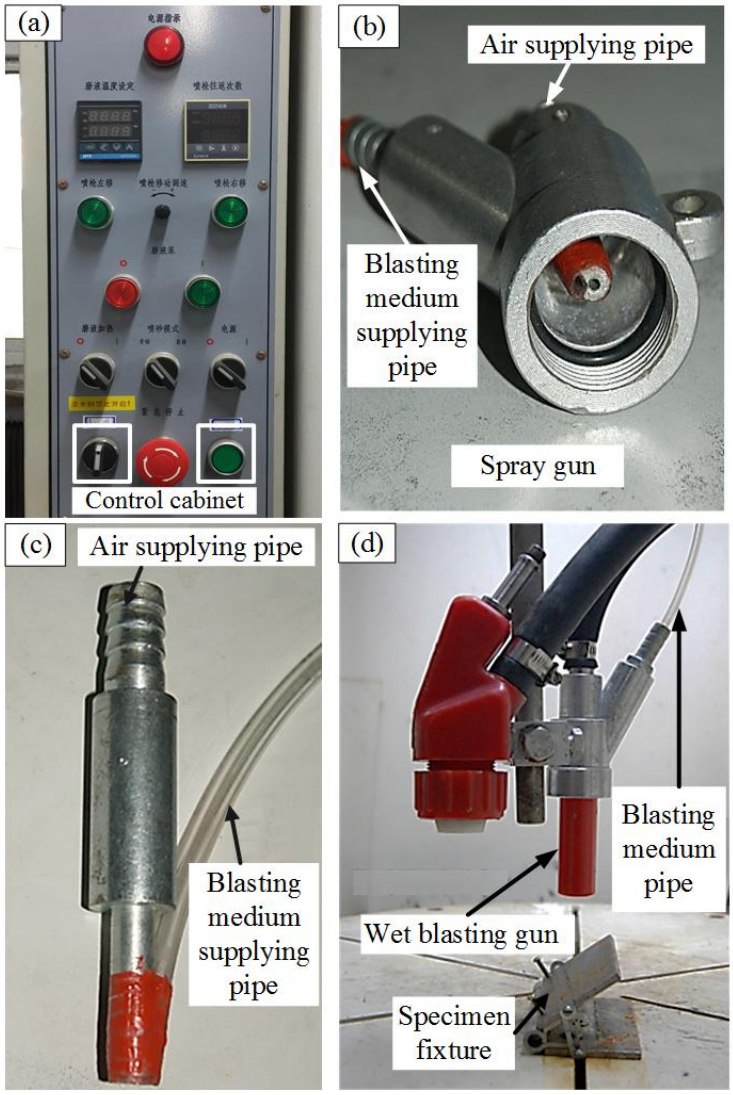

Fig. 4.5 Reconstructed apparatus in the liquid blasting test rig

(a) – Control cabinet, (b) – Installation of pipes inside the spray gun, (c) – Air and grit supplying pipes, (d) – Assembled spray gun

Chapter 5

Oily Contaminant Cleaning

Decommissioned engines are usually contaminated by mixtures of organic and inorganic compounds, covering the surface and internal walls of different parts. Fig. 5.1 is a decommissioned Dtyer™ Heavy Duty Engine (WD615-48C/21) photographed in Sinotruk Jinan Fuqiang Power Co., Ltd. in China. Study surrounding contaminations of retired engines were all offered by this company, disassembled from this type of engines.

Fig. 5.1 Polluting conditions on a decommissioned Styer engine assembly

On the surface of decommissioned engines can be usually observed oily and rusty contaminations, carbon depositions, paint layers and dust accumulations. The

engine internals were contaminated by oily contaminations and carbon depositions, from lubricating oil, leaked fuel and carbons due to incompletely combustion (García-Cascales and Lamata, 2009).

5.1 Analysis of Contamination Layers

Modern analysis technologies and facilities could help obtain physiochemical information of the contaminations including surface morphology, elemental compositions and specific functional groups in the contamination molecules. However, contaminations are usually complex mixtures (Widera and Seliger, 2015) from different working environments (Heremans et al., 2005) and it is difficult to obtain full information of contamination.

Organic liquid compounds and carbon depositions are the most commonly observed contaminations. Surrounding this, studies (Korus et al., 1985) had been conducted on the rate of carbon deposition on direct injection diesel nozzles when various ratios of vegetable oil was used as fuels. According to the different electrical conductivity of compound in contaminant, a method was proposed to determine contaminant contents in diesel engine oil using electrical conductivity measurements at different frequencies (Heremans et al., 2005). Yet, the study could not describe the chemical compositions of contaminations from different working conditions. To monitor the composition changes in lubricating oils, Fourier Transform infrared (FTIR) spectroscopy was proposed as a reliable method that was able to monitor the degradation products and non-metallic contaminants, as well as oxidation (Wiseman and Ah-Sue, 1992, Obiols, 2003). The addition of scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS)

could supply more detailed changes in the micro morphology and chemical ingredients of the contamination (Guan et al., 2013) . The compositions of oily contamination layers on a heavy diesel engine piston could be investigated through FTIR, X-ray diffraction (XRD) and transmission electron microscope (TEM) methods (Smith et al., 2002), as illustrated in Fig. 5.2. The composition of the contamination layers was associated with running durations and lubrication types, usually containing Ca and Zn phosphates.

In this research, the FTIR technology has been used to analyse the compositions in contaminants from different part of an engine, to validate the feasibility of SC-CO_2 cleaning as the alternative solvent.

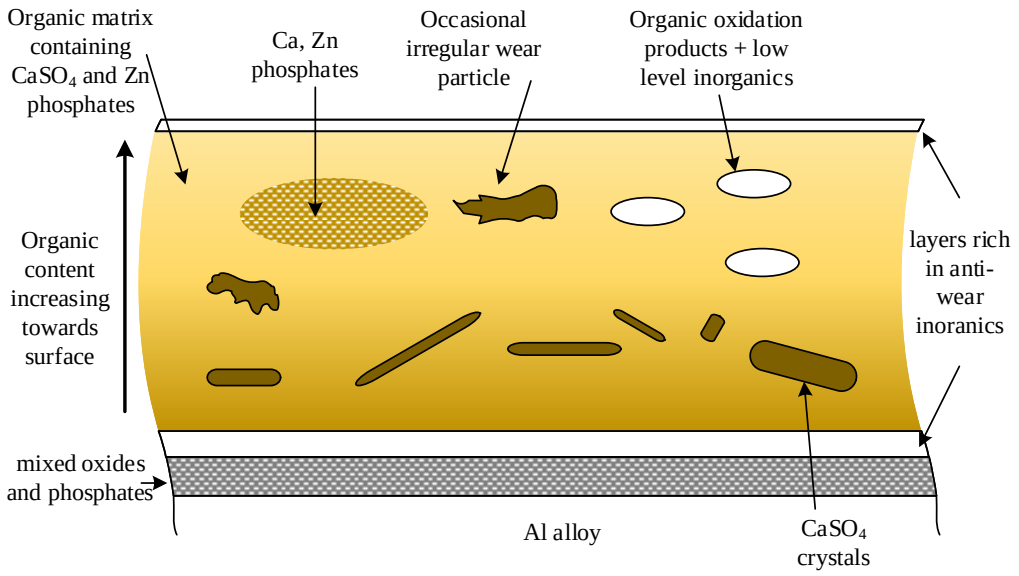

Fig. 5.2 Schematic diagram of a contamination layer from a typical heavy diesel engine piston (Smith et al., 2002)

5.1.1 Macro Observations

A piston is one of the most significant parts of an engine, primarily transmit propulsions generated through fuel combustions to pins and crankshafts. Due to the strict working environment, there could be a layer of carbon deposition on the decommissioned piston head, as illustrated in Fig. 5.3. A piston head composes one part of the chamber, where incomplete combustions could occur, giving rise to gums and asphaltenes. Oily sludge and residual liquid oil could be also observed on the piston skirt areas.

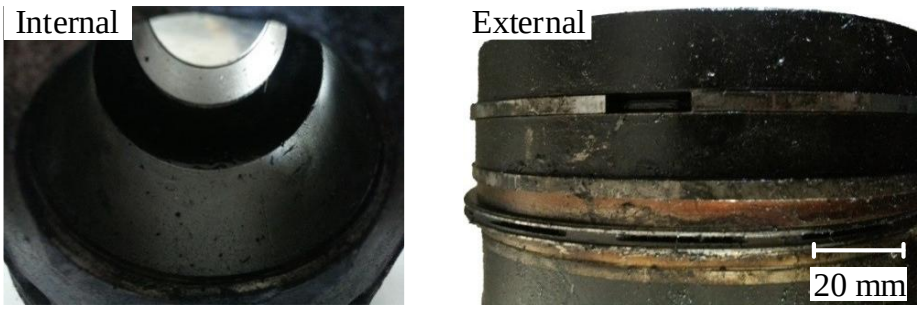

Fig. 5.3 Carbon deposition layers on and inside a decommissioned piston head

Valves are responsible for intaking fresh air and exhausting combusted gases in an engine. During direct contact with the combustion chamber in severe working conditions, apparent carbon depositions were observed on the head surface of the valve, as shown in Fig. 5.4 (a). On the underhead areas in photograph (b), there were massive carbon depositions adhering to the surface by very strong adhesive forces. It was very difficult to thoroughly remove those contaminations using conventional physical cleaning methods. On the valve stem, the oil pollution was less in the region near to the underhead, while the oxidation on the substrate

materials was serious, induced by the high temperature occurring in this area from the combustion chamber.

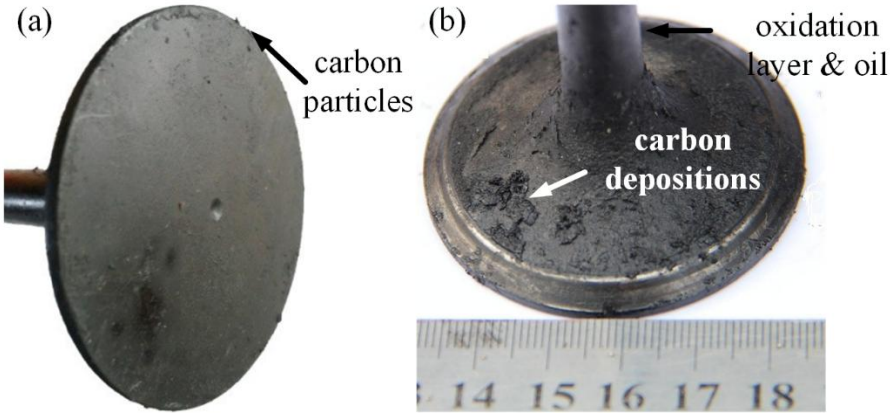

Fig. 5.4 Carbon distributions on a valve; (a) – head surface, (b) – underhead and valve stem

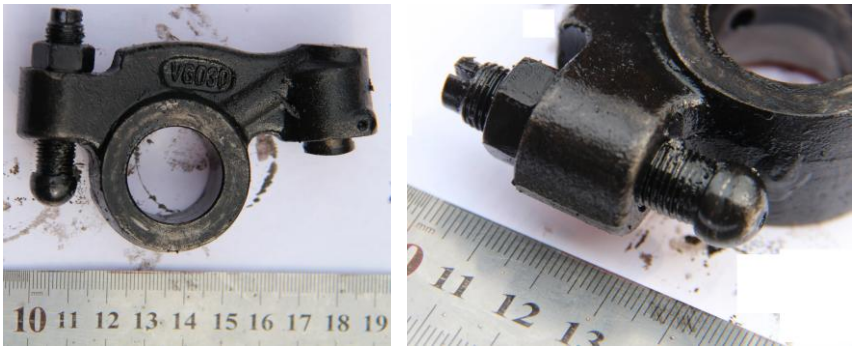

Fig. 5.5 Polluting conditions on rocker arms

Fig. 5.5 photographs polluting conditions rocker arms from decommissioned engines. There were oily and greasy contaminations broadly distributing on the surfaces of those parts. These contaminations were mixture of dusts, metallic particles and lubricating oil and its degradation products, among which liquid compounds such as oil and lubrication could increase the adhesive forces between particles the substrates (García-Cascales and Lamata, 2009) through the capillary

effects.

Further study into the ingredients and structure of contamination layers of an engine employed microscopy, FTIR spectra and elemental analysis in the following content.

5.1.2 Microscopic Observations

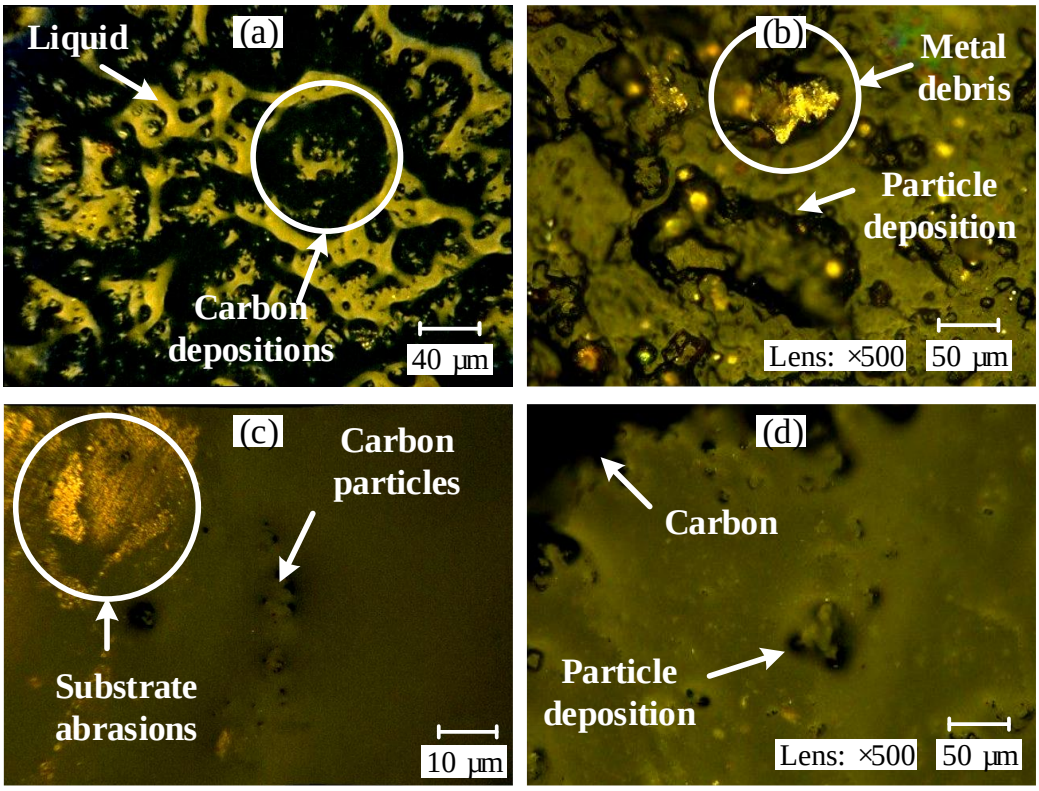

Fig. 5.6 Morphology of carbon depositions and oil residuals on different parts

(a) – valve, (b) – heat shield, (c) – rocker arm, (d) – nut

Fig. 5.6 were images of contamination morphology from different parts of an engine, photographed by an ultra-depth microscopy (VHX-600, keyence, Japan).

There were carbon depositions adhering to the valve and heatshield, as illustrated in Fig. 5.6 (a) and (b). The dark areas in the images were carbon depositions that absorbed the illuminations of the microscopy. In contrast, the bright areas are the reflection of light by the liquid compounds in the carbon depositions. Absorbing on the substrates by a strong adhesive force layer by layer, carbon depositions became contamination that was very difficult to remove. In Fig. 5.6 (b), metal debris mixed with the carbon particles could also be observed. With the coexistence of lubricant in liquid status, some carbon depositions turned into solid or gum-like condition, adhering to the substrates by strong forces, increasing the difficulty of thoroughly removing them by a single cleaning operation. Comparing with carbon depositions, oil residual layers, in Fig. 5.6 (c) and (d), had a smoother appearance, looser structures and clearer textures, which imparted the contaminants a much lower hardness. The oily contaminations were thin compared to carbon depositions, through which the substrate abrasions could be observed on the rocker arm in Fig. 5.6 (c). It was much easier to clean the liquid contamination layer while the existence of liquid could induce capillary forces on the surface, consequently increasing the probability of particle adhesions and accumulation on this layer.

5.1.3 FTIR Analysis

Oily contaminants in an engine are mixtures with complex ingredients, containing lubricating oil, its deterioration products after long term running, moisture, dusts, metal debris, leaking fuels and carbon depositions. In addition, the polluting conditions and contamination compounds also varies in engines from different working environment. The inhomogeneity of contamination had

seriously restricted the further study on compounds of engine contaminations.

Lubricating oil manufacturers always add additives into the base oil to achieve the specific working performances. These additives are commercially confidential information with patent protections, consequently increasing the difficulty of analysing lubrication ingredient. Therefore, in contrast with the analysis of pure matters, it is extremely difficult to obtain precise compositions of one lubricating oil. In this research, FTIR spectroscopy had been used to analyse compositions of lubricating oil and contaminations of different kinds. Fig. 5.7 gives the infrared spectra of new lubricating oil, oily contaminations and carbon depositions. Using the *Peak Analyzer* tool in Origin (2018b, OriginLab, USA), hundreds of peaks were marked ranging from wavenumbers 4000 to 500 cm^{-1}. It was very difficult to analyse the hundreds of peaks from the FTIR spectra comparing with those of pure substances; however, it was still possible to see the existence of some specified functional groups and distinctions between different substances. Peaks at wave numbers of 2923 and 2854 cm^{-1} demonstrated the existence of saturated hydrocarbon bonds ($-CH_2-$); at 1459 and 1376 cm^{-1} were the deformation vibrations of methyl ($-CH_3$) in the samples. The right areas are the fingerprint region (1330 – 400 cm^{-1}) with complex spectra that illustrated the subtle changes inside the molecules. Every organic compound has a particular spectrum in this region, varying in the peak positions, transmission percentage and spectrum shapes. The peaks at 723 cm^{-1} in this region could demonstrate that there are aliphatic hydrocarbons $(-CH_2-)_n$ ($n > 4$) in the contaminants. Base oil in a lubrication usually accounted for 70%-99% by weight. Base oil content in the lube chosen was about 80% alkanes. Comparing the spectra, the contaminants has more peaks at the other

wave numbers in the fingerprint region, demonstrating that in the oil contaminations and carbon depositions existed other compositions apart from lubricating oils.

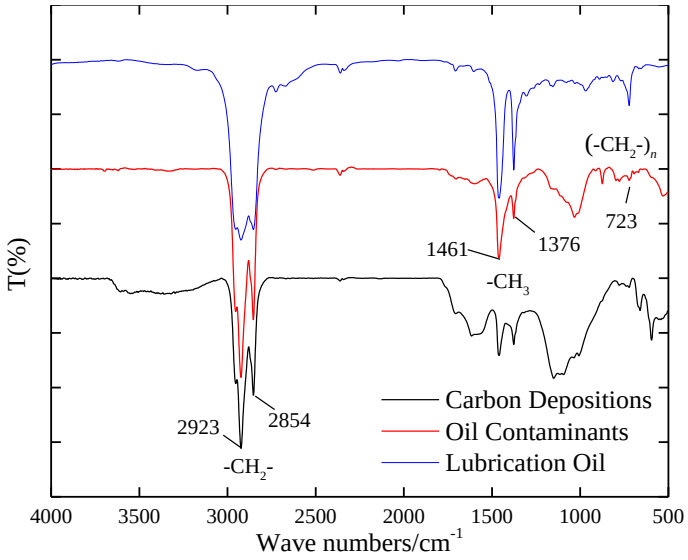

Fig. 5.7 Infrared spectra of lubricating oil and contaminations of oily and carbon depositions layers

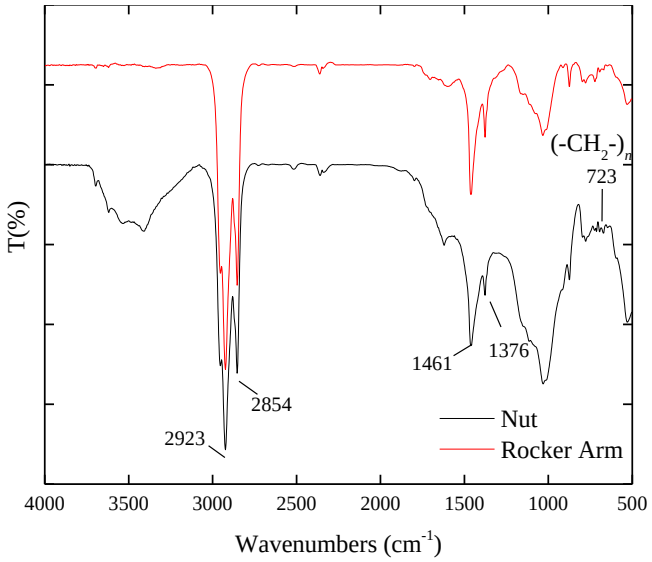

Fig. 5.8 Infrared spectra of oily contaminations from nuts and rocker arms

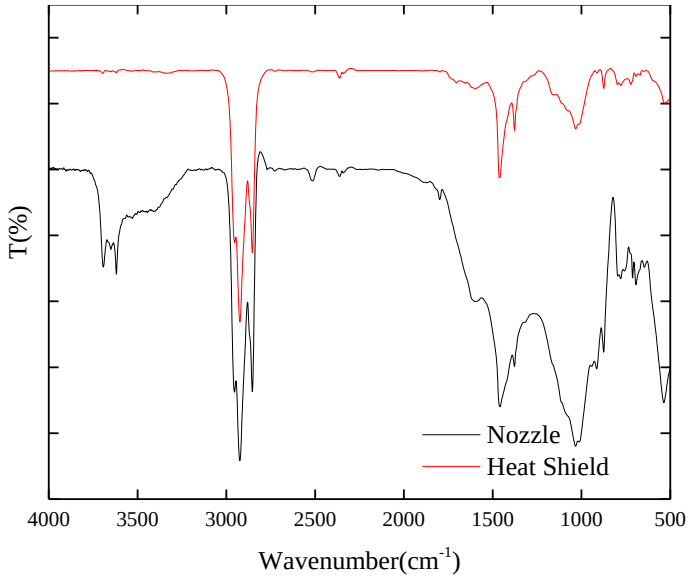

Fig. 5.9 Infrared spectra of carbon depositions from nozzles and heat shields

Fig. 5.8 and Fig. 5.9 illustrates the spectra of carbon depositions and oil contaminants from different positions of an engine. Four spectra showed similar peaks comparing with Fig. 5.7; however, the characteristic peaks in the fingerprint areas were quite different. The presence of peaks at 2923, 2854, 1461, 1376 and 723 cm^{-1} could only explain that there was base oil in those contaminants. Based on the FTIR analysis of lubricating oil and contaminations of different kinds on an engine, it can be deduced that SC-CO_2 could have the effect of removing extractable compositions in the contaminants, consequently weakening the adhesive forces between the residues and substrates for post-treatment.

5.1.4 Elemental Analysis

Table 5.1 shows the elemental analysis of two typical types of engine contamination using an elemental analyser (varioEL-III, Elementar, Germany). It

demonstrates consistent results with the FTIR spectra that organic substances accounted for the majority of the contamination through the mass ratio of carbon and hydrogen elements. However, the simple analysis cannot give more information on the contamination ingredients. Consequently, energy dispersive spectrometer (EDS) and electron probe micro-analyser (EPMA) were used for further analysis of contamination.

Table 5.1 Weight percentage of C and H in contaminants from different positions

Contamination Type	Positions	C content/wt%	H content/wt%
Carbon Depositions	Nozzles	38.6	3.52
	Retaining Rings	52.32	4.409
Oily Contaminations	Nuts	26.12	3.688
	Rocker Arms	42.89	4.707

EDS sampling was carried out and replicated five times, on the highlighted region of a carbon particle, as illustrated in Fig. 5.10. Test results demonstrated that the major elements in this sample were C, O, Al and Si, etc., among which proportion of the Carbon was as high as 70.79%, mainly in the form of unburned carbon depositions. The detected Phosphorus and Sulphur might be from incompletely burned fuel or the additives of lubricating oil, transforming into compounds adhering to the substrates under alternately changing temperatures. The exhibited Silicon in the contaminations primarily came from modifiers in the lubricating oil and intaking dust particles through valves, while metallic elements such as Fe, Al and Zn were from debris due to unexpected abrasions between engine parts.

The EPMA method was usually used as a supplementary for quantitative analysis of one substance. In this study, EPMA was used as well with the result being shown in Fig. 5.11, verifying the previous analysis results.

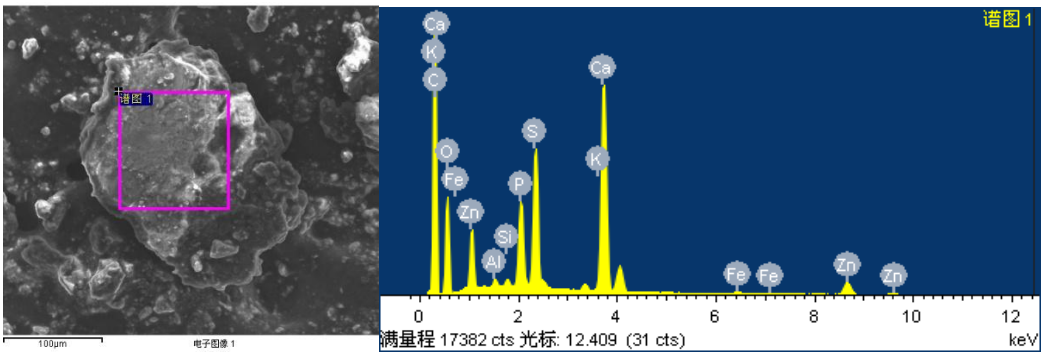

Fig. 5.10 Sampling area for EDS and the corresponding spectrum

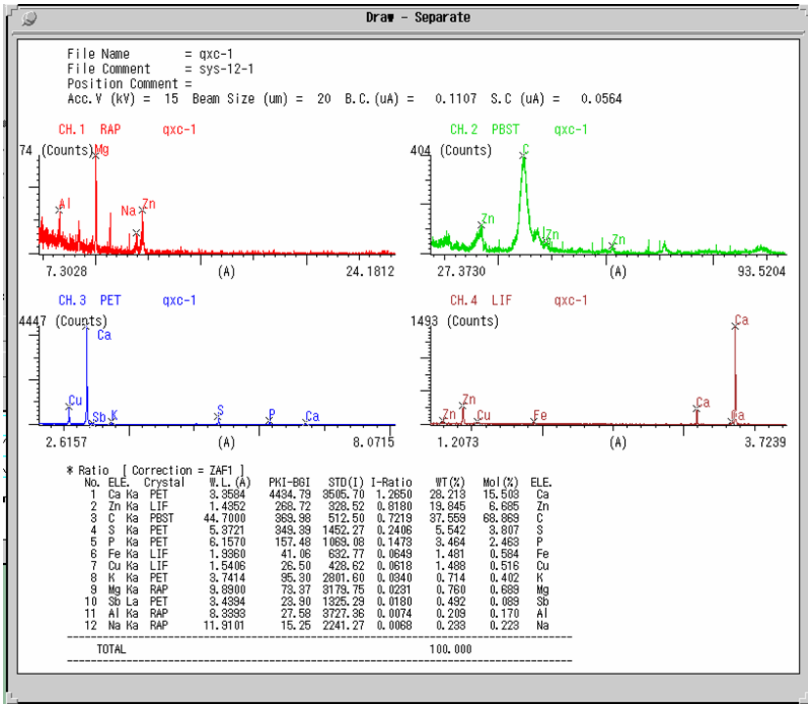

Fig. 5.11 Quantitative analysis of EPMA from carbon depositions

Table 5.2 Elemental analysis by EDS

Elements	Weight Percentage/wt%	Atomic Percentage/%
C K	56.27	70.79
O K	22.12	20.89
Al K	0.19	0.10
Si K	0.15	0.08
P K	2.70	1.31
S K	4.39	2.07
K K	0.26	0.10
Ca K	9.79	3.69
Fe K	0.28	0.07
Zn K	3.86	0.89
Total	100.00	/

5.2 Lubricating Grease Cleaning

Lubricating greases widely distribute on different parts of an engine, including pistons, cylinder heads, crankcases, etc.; therefore, qualitative and quantitative experiments were carried out on lubricating grease cleaning.

5.2.1 Qualitative Experiment Study

Qualitative experiment was initially carried out on the lubricating grease cleaning in SCF cleaning test. Contaminants for the cleaning test were selected based on the criterion that after SCF cleaning operations, there should be a measurable quantity of residues under some conditions in the range of test parameters. Therefore, the cleaning test chose a mineral lubricating grease which was usually used in bearing lubrications, containing hydrocarbons (paraffinic mineral oils), thickener (mixture of ethylene-propylene copolymer and ethylene-propylene-ethylidene norbornene terpolymer) and a small percentage of amine-

based antioxidant additives, as the contaminant specimens. Considering the good adhesion and extremely low mobility of greases, galvanized patches were used as the carrier in the SCF test. After coating with greases, metallic patches were hung and air-dried for two days under the sunlight, through which contaminants would be more compacted to resemble actual contamination.

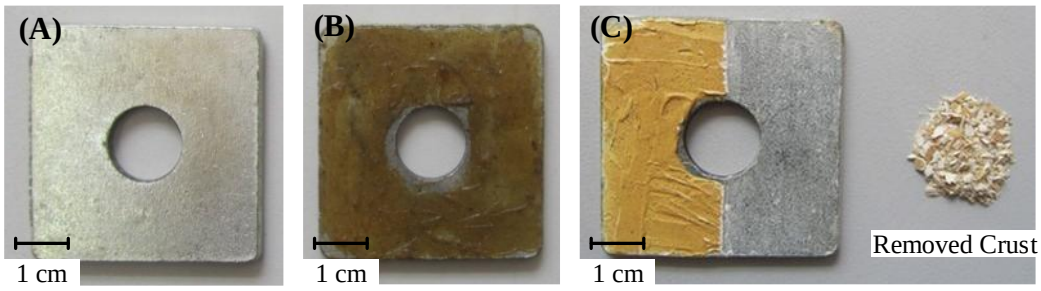

Fig. 5.12 Comparisons before and after SCF cleaning on lubricating greases

Images in Fig. 5.12 show the appearances of metallic patches prior to (Fig. 5.12 – A) and after (Fig. 5.12 – B) being coated with lubricating greases and the effect of SCF cleaning, respectively. The semi-transparent greases in Fig. 5.12 – B became opaque and the soft texture turned into a very solid layer after being treated in the SC-CO_2 atmosphere. The remaining solidified scale crust could be much more easily removed than the original layers by operations e.g. polishing, as illustrated in Fig. 5.12 – C. The changes in transparency may be caused by the loss of soluble compounds extracted from the greases into CO_2 fluids, leaving the internal structure of grease layer with holes which were invisible to the naked eye while able to block the spread of lights in grease layers.

5.2.2 Gravimetric Analysis

The cleaning capacity of one method could be evaluated by gravimetric

analysis approaches. In the SCF cleaning study, an analytical balance with 0.1 mg readability was used for gravimetric analysis. For each set of experiments, the metallic patches were of a same size (40 mm×40 mm×2 mm) with a hole in the centre. The mass of the contaminant in the experiment was controlled within ±1 g from run to run.

Experiments investigated the cleaning effect by regulating the cleaning temperature, vessel pressure and cleaning time. The samples were weighted prior to coating, after coating and after cleaning operations. Decontaminating effects were evaluated using the following equations

$$m_C = (m_1 - m_0) - (m_2 - m_0) = m_1 - m_2 \tag{5.1}$$

$$CPI = \frac{m_C}{m_1 - m_0} \times 100\% \tag{5.2}$$

where m_C (g) is the decontaminating amount; CPI (%) is the cleaning performance index (van Roosmalen et al., 2003a), i.e. decontaminating rate in this study; m_0 (g) is the mass of the metallic patches; m_1 (g) is the mass of patches after being coated with greases and m_2 (g) represents the weight of samples after SCF cleaning. Data used in statistical analysis were mean values of three duplications in each operation.

The effects of cleaning time, pressure and temperature was investigated in the gravimetric study. Fig. 5.13 shows the comparison of removal rate curves at cleaning pressure of 20 MPa with cleaning temperatures ranging from 50 °C to 70 °C. The samples were taken out and weighed every thirty minutes, from 0.5 h to 3 h, to log the removal rate variations. Similar experiments had also been carried

out for pressures variations, which is illustrated in Fig. 5.14. It could be read from the curves in Fig. 5.13 that removal rates increased significantly in the beginning stages of the cleaning operation and plateaued at approximately 43%, after 2.5-hour treatment in the SCF. The sample with maximal cleaning capacity was the one treated at temperature of 70 °C within the experiment range. At the initial stages, the increment of temperature could accelerate the cleaning process. However, removal rates at different temperatures eventually came to a similar cleaning result, demonstrating that temperature could increase cleaning efficiency while not affecting the eventual removal rate when cleaning duration was adequately long.

The impact from pressure on the removal rate was analogous to that from temperature. As illustrated in Fig. 5.14, removal rate presented a dramatic inclining trend with increasing pressure at the initial stages, while the ultimate rates were similar at around 42% after cleaning for 3.0 hours. It could be concluded that the cleaning efficiency at the initial stages could be promoted by increasing operation temperatures and pressures, yet not the eventual cleaning capacity. When SC-CO_2 was used for the cleaning of lubricating greases, there would be massive residues left on the cleaning objects. Subsequent removal operations are required for a better cleaning result.

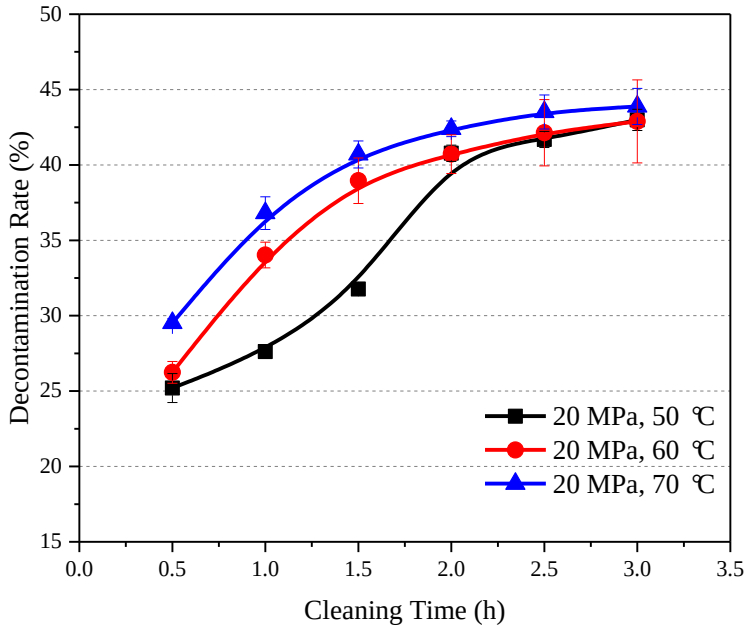

Fig. 5.13 Decontamination rate comparison for varying cleaning temperatures

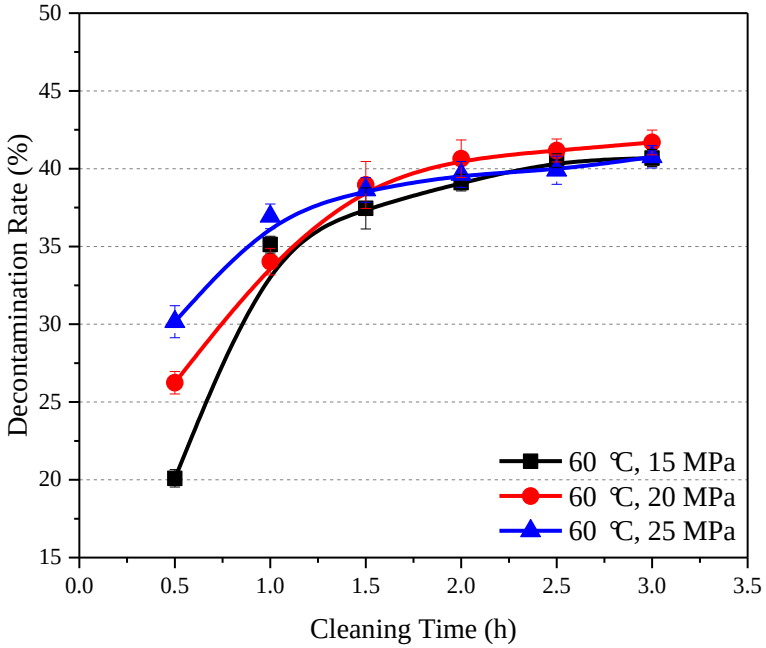

Fig. 5.14 Decontamination rate comparison for varying cleaning pressures

The ultimate decontamination rate was 1 % higher at a higher temperature in the grease cleaning by use of SC-CO_2. Primarily, the viscosity of the greases was low at a high temperature, which facilitated the dissolution process. Moreover, the results indicated the existence of additives clustering on the interface between greases and SCF, which eliminated at an increasing temperature and promoted the penetration of CO_2 molecules into the grease layers.

5.3 Factorial Study in Lubricating Oil Cleaning

Cleaning operations in remanufacturing are faced with various kinds of contaminants, among which the oily contaminant is one of the most commonly observed. However, the contaminants on retired engines were difficult to collect and they would bring pollution to the test rig after excessive batches of cleaning. According to the analysis of contaminants in 5.1, lubricating oil was used as the "contaminants" to investigate the parameter optimisation in SCF cleaning using CO_2.

5.3.1 Ingredient Analysis

The extracted oils from engine contaminants presented darker colours than the new motor oil (lubricating oil) HPO TURBO SG/CF-4 5W30, from the comparison between the two substances in Fig. 5.15, demonstrating the ingredient changes from lubricating oils to the liquid compounds in the contaminants. Motor oils today are blended with base oils that are composed of hydrocarbons, poly-alpha-olefins and poly-internal-olefins (Shubkin, 1993); some high-performance motor oils however contain up to 20% esters by weight (Schlosberg et al., 2001).

The darker colour was from those small molecular carbon depositions which could dissolve in the liquid oil. The FTIR spectra in Fig. 5.16 could demonstrate the differences between original lubrication oils and the liquid oil compositions from contaminants. Extra peaks were observed at wavenumber of 2727, 2360, 1706 and 1604 cm^{-1}. These differences, together with the waveform changes shown in the rectangle regions, could prove the chemical changes between new lubes and oil contaminants.

Fig. 5.15 Comparison of extracted oil from contaminants (left) and new lubricating oil SG/CF-4 5W30 (right)

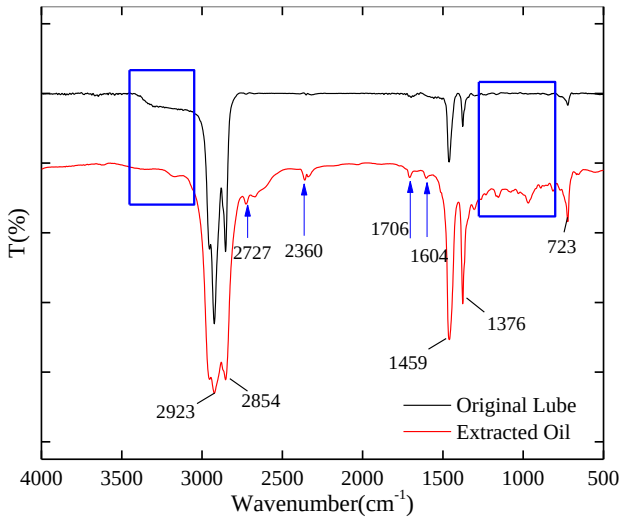

Fig. 5.16 Infrared spectra of lubricating oil and contaminations of oily and carbon depositions layers

5.3.2 Experiment Procedures

The method of preparing grease contamination samples was not feasible for making contaminant samples in the study of lubricating oil cleaning because the oils had a higher flowability in contrast with lubricating greases. For the statistical and experimental convenience, oil absorbing pads were used as the substrates that carried liquid lubes, with the size of 100 mm × 100 mm × 2 mm, as illustrated in Fig. 5.17. The oil-saturated pads were subsequently hung in a ventilated place to drain excessive liquid compound in the absorbent pads and stabilise the contaminant mass among each operation. Carbon dioxide is of 99.8% purity in this experiment. Gravimetric analysis methods in Eqs. (5.1) and (5.2) were used to evaluate the cleaning capacity of SC-CO_2 cleaning. Repeatability of the experiments was guaranteed by replicating cleaning tests three times for each cleaning parameter and weight data were the mean value of three individual measurements in every test.

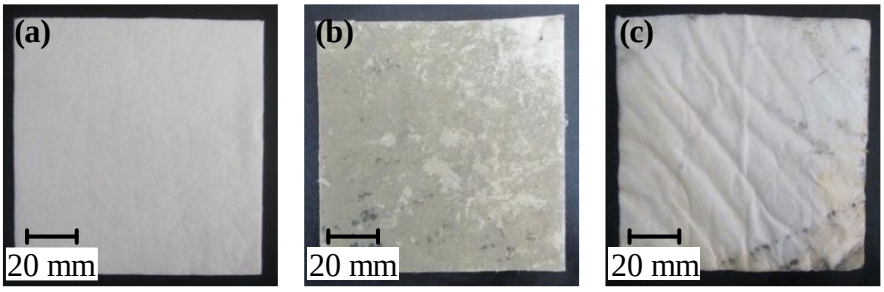

Fig. 5.17 The appearances of absorbent pads prior to and after SC-CO_2 cleaning

(a) – original absorbent pads without lubricating oil, (b) – oil contaminated and air-dried pads, (c) – absorbent pads after SC-CO_2 cleaning

By controlling the different temperatures and pressures in the two separators,

the density of CO_2 fluid was decreased dramatically from supercritical (cleaning vessels) to gas (separator-1 and 2) status. Contaminants dissolved in SC-CO_2 entered separator-1 along with CO_2 and were then separated from the fluid by decreasing its temperature and pressure. Therefore, the contaminants could be collected at the drain outlets of separators and the CO_2 was reclaimed for recycling.

This study investigated the effects of parameters of cleaning durations, outflow rate of CO_2 fluids, operating temperatures and pressures on the eventual cleaning results. Temperature in this test ranged from 35 °C to 105 °C with pressure in the range of 10 MPa to 30 MPa. From the literature, SC-CO_2 had been previously used as the solvent to extract and reclaim oil from machining wastes (Fu and Matthews, 1999). Results demonstrated that only 3 % increment were achieved in the removal rate when flowrate increased from 0.2 to 0.6 ml/s. In the experiments, it was assumed that flow rate was an independent factor to the final oil removal rate. Accordingly, experiments surrounding parameters that had seemed to be more crucial in increasing the final decontamination rates were carried out at a flowrate of 1.33 ml/s to clean for 30 minutes. Study of cleaning durations and flowrate was based on the results from temperature and temperature trials.

5.3.3 Effect of Pressure

For the study of pressure on the final decontamination rate, eight levels of pressure were investigated in the experiment, i.e. 7.5, 8.5, 10, 14, 18, 22, 25 and 30 MPa, with the experiment results shown in Fig. 5.18. For the convenience of reading, the statistics that were demonstrated in Fig. 5.18 (e) was divided into four

separate graphs from Fig. 5.18 (a) to (d). At the same residence time in the cleaning vessel, the decontamination rate could present the cleaning capacity of SC-CO_2 at different conditions. In comparison with that of grease cleaning, the decontamination rate for the oily contaminants was much greater, as high as 90% at a feasible condition. As expected, the decontamination rate, i.e. cleaning capacity, increased with pressure when the temperature was set at a given value.

Comparing Fig. 5.18 (a) to (d), the increment of decontamination rate at lower pressures were not significant. However, decontamination rates would go through a drastic increment when the pressure continued to increase and eventually plateaued when the pressure went up to 25 MPa. At different temperatures, a sharp increment occurred in different pressure intervals. Starting pressures for sharp increment gradually increased with temperatures, leading to a higher decontamination rate at a higher temperature as well. This phenomenon was especially apparent in Fig. 5.18 (a), where the sharp increment in the 35 °C curve happened from the lowest pressure (7.5 MPa) while at 45 °C, it went through a steady phase from 7.5 to 8.5 MPa. An overall comparison could be apparently referred to from Fig. 5.18 (e); the higher pressure was used, the greater decontamination rate showed the SC-CO_2. The cleaning capacity was primarily determined by the solubility of contaminants in the solvent, which was intrinsically associated with the interactions between solvent and solute molecules and reflected by the correlations of solubility and solvent bulk density. By increasing its pressure, the density of SC-CO_2 was increased, consequently increasing the cleaning capacity in SCF cleaning operations. In the vicinity of the critical point, a slight pressure change could lead to dramatic density variations, presenting as a

sharp increment of decontamination rates in Fig. 5.18. The reason that initiating pressure was postponed by increasing temperature would be explained specifically in 5.3.4.

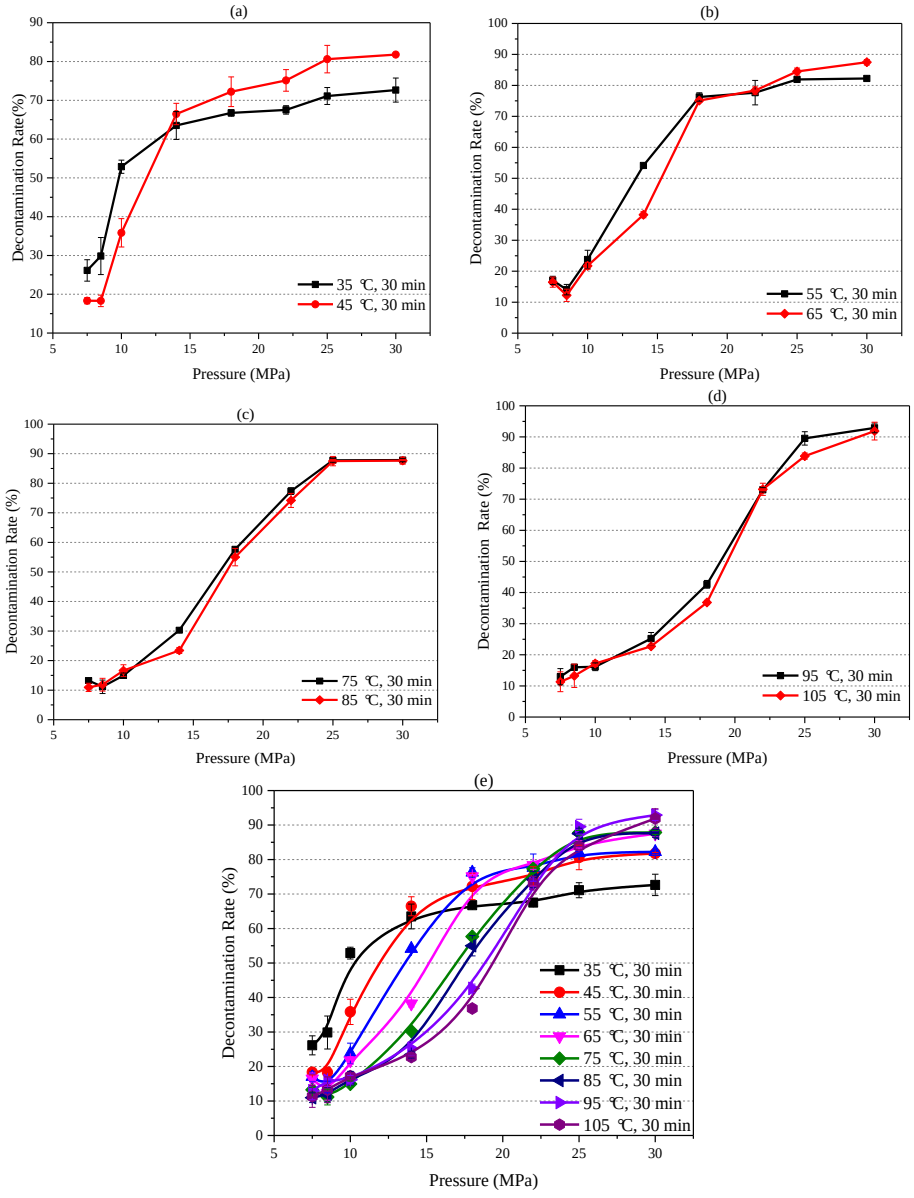

Fig. 5.18 Effect of pressure on the decontamination rate of SC-CO_2 cleaning at different temperatures (a) – 7.5 and 8.5 MPa, (b) – 10 and 14 MPa, (c) – 18 and 22 MPa, (d) – 25 and 30 MPa, (e) –the whole test range

5.3.4 Effect of Temperature

Fig. 5.19 depicted the decontamination rate curves carried out at different temperatures, from 35 °C in ten-degree increments to 105 °C, under constant pressure conditions. Pressure had a positive effect on the cleaning capacity of SC-CO_2 by increasing the fluid density; however, the temperature had more complicated impacts on the result of cleaning capacity. Fig. 5.19 (a), (b) and (c) demonstrated different trends from Fig. 5.19 (d), in which temperature had a positive impact on the decontamination rate of SC-CO_2. At a relatively low pressure, from 7.5 to 10 MPa, decontamination rates demonstrated a negative effect on the increasing temperature. At the pressures ranging between 14 and 22 MPa, the impact of temperature was not as linear as that at lower pressures. Under the fixed pressure and cleaning durations, decontamination rates in this range firstly increased with the temperature and then showed a declining trend. The peaks of the decontamination rate in each line were found to be different under different operating conditions; the higher pressure was used the higher temperature was the peak at. Decontamination rates, at the two high pressures in the test range, were in the positive correlations with temperatures and could surpass 90%.

Temperatures had two aspects of impact on the solubility of one contaminant in a SCF. By increasing the temperature in the supercritical system, on the one hand, there would be less molecules contained in a fixed-volume vessel at a given pressure, resulting in the declining of the bulk density of a SCF and negatively affecting the cleaning capacity. On the other hand, however, the increment of temperature could improve the volatility of solvents and solutes. The overall effect of temperature in a SCF cleaning system was determined by the both aspects. If

the increment of contaminant volatility was significant at a higher pressure, the cleaning capacity would present a positive correlation with temperatures. On the contrary, higher temperatures reduced the eventual cleaning capacity on the occasion that the vapour pressure of contaminants in SC-CO_2 fluids did not vary considerably with the temperatures. It could be concluded from Fig. 5.19 (a) that the volatility of oil contaminants in this test did not change severely with temperatures. Violent changes in cleaning capacity were found at temperature in the vicinity of the critical point. At lower pressure, the negative impact of temperature on the removal yield prevailed, while the positive impact from increasing pressures gradually surmounted that from the temperatures, explaining the existence of peaks in the line Fig. 5.19 (b) and (c). At a higher pressure of 25 and 30 MPa, the solubility increments augmented by increased density could surmount the negative impact from temperatures, showing a straightforwardly increasing trend between temperatures and decontamination rates.

In general, temperature improved the volatility of contaminants in the SC-CO_2 fluid and accelerated contaminant desorption. However, the negative roles it played was also significant in decreasing the solvent density. From the graphs in Fig. 5.19, it could be concluded that suppressions from temperature prevailed at a low pressure while density and solubility increase dominated the overall properties exhibited in the cleaning process.

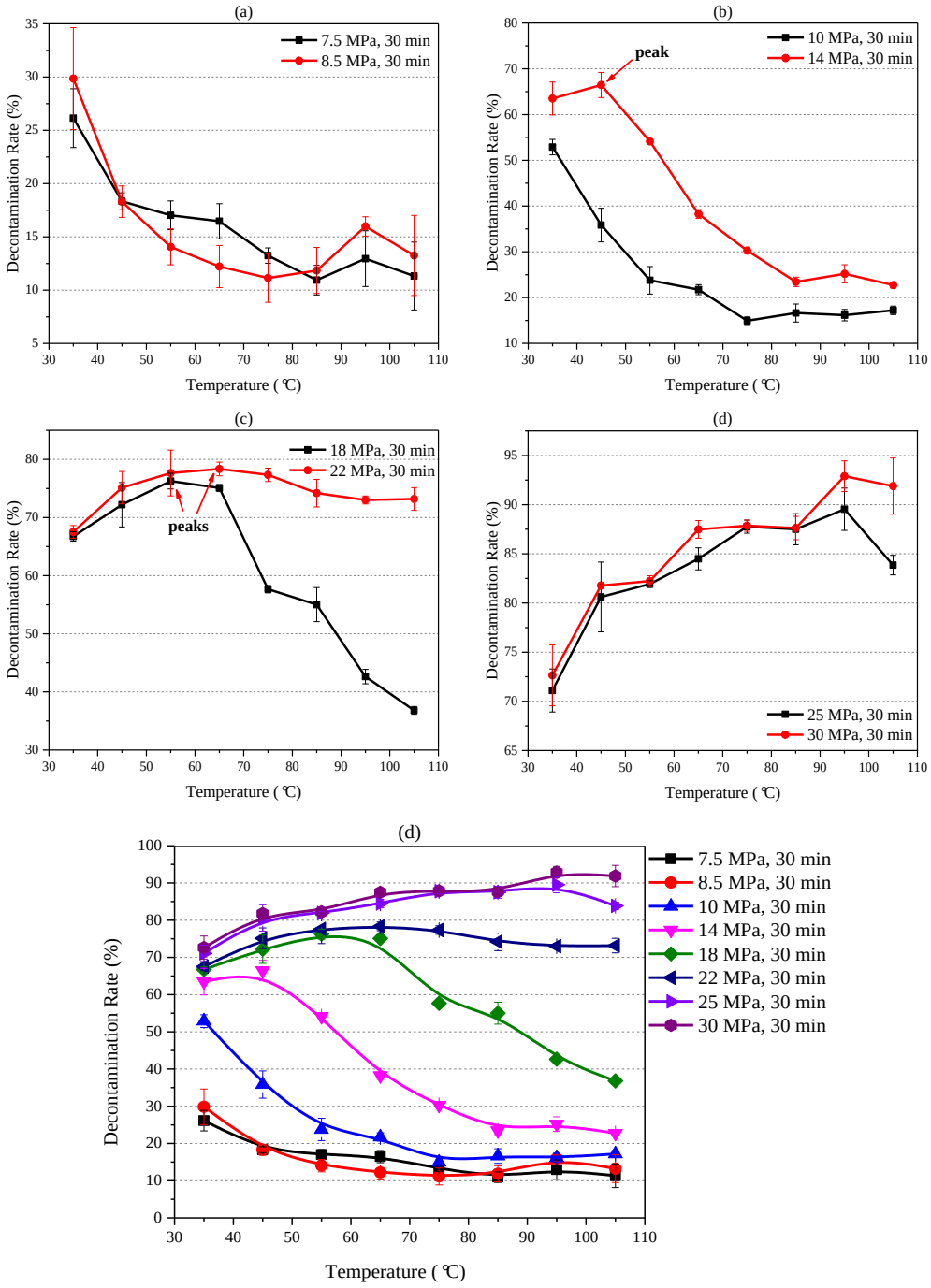

Fig. 5.19 Effect of temperature on the decontamination rate of SC-CO_2 cleaning at different pressures; (a) – 35 and 45 °C, (b) – 55 and 65 °C, (c) – 75 and 85 °C, (d) – 95 and 105 °C, (e) – the whole test range

5.3.5 Effect of Cleaning Time

The cleaning time could significantly influence the eventual cleaning results in SC-CO_2 cleaning operations. It is therefore necessary to investigate the impact of cleaning duration on the decontamination rate, when all the other parameters were fixed at given values. Temperature and pressure in this part were set at 65 °C and 22 MPa respectively, based on the outcomes obtained from 5.3.3 and 5.3.4, with a same flow rate of 4.8 l/h (frequency of the pumps was 40 Hz).

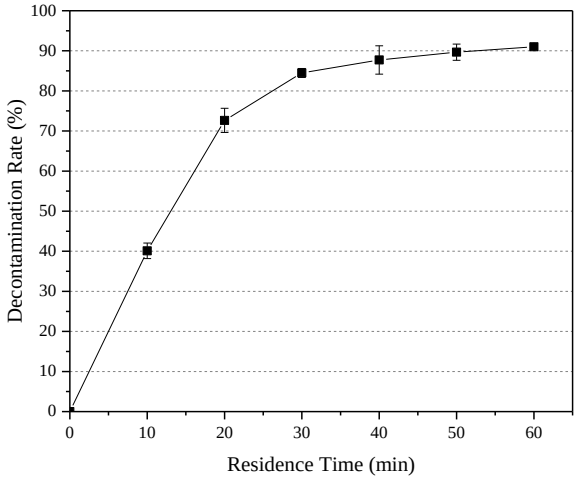

Fig. 5.20 Decontamination rate changes against different residence time in SC-CO_2 cleaning

Fig. 5.20 shows the effect of residence time on decontamination rate changes in the cleaning vessel. It is apparent that the overall decontamination rate curve could be divided into three stages in this experiment, similar with extraction process using SC-CO_2; the linear stages in the initial period (0 – 20 min), slow increasing in the second period (20 – 50 min) and the plateau attained period in the final progress (50 – 60 min). As expected, prolong the residence time increased the

decontamination rate; the longer the cleaning time was, the more chances contaminant substances could get in contact with SCF. The increased solvent penetration deeper into the contamination layers allowed a greater amount of mass transfer developing between the interface of SCF and contaminants. However, with dissolving progressed in SCF, the concentration of the soluble compound in contamination gradually levelled off, resulting in very little changes in decontamination rates after 40 min. There could be observed minimal increment when cleaning time was increased from 40 min to 60 min. Considering the overall effect of cleaning results and energy consumptions, it was suitable to use 30 min cleaning residence time for pure SC-CO_2 cleaning.

5.3.6 Effect of Flow Rate

The flow rate was also a significant parameter affecting the efficiency of SC-CO_2 cleaning. When the other parameters were fixed at constant values, a low flow lead to longer residence time for SC-CO_2 fluid in the cleaning vessel, which allowed fluid to remain in contact with and diffuse into the contamination layers and consequently increase the cleaning capacity of SC-CO_2 (Saldaña et al., 2010). When the flow rate of SC-CO_2 was too low, there would be insufficient amount of CO_2 going through the cleaning vessel, which consequently impeded the dissolving of contaminants into SC-CO_2 and resulted in a low cleaning capacity (Topal et al., 2006). Increasing the flow rate could increase the cleaning capacity of SCF by increasing the amount of CO_2 molecules in the vessel and intermolecular interactions with contaminants. However, the velocity of fluid was also increased with the increasing flow rate. At a high velocity, CO_2 molecules were forced to go through the vessel with less time, so, instead of penetrating into

contaminants, SC-CO_2 flowed around them and through the channels, limiting the contact time for dissolution. In this experiment, the ultimate effect of flow rate on the decontamination rate is shown in Fig. 5.21. The decontamination rate increased with the increasing flow rate.

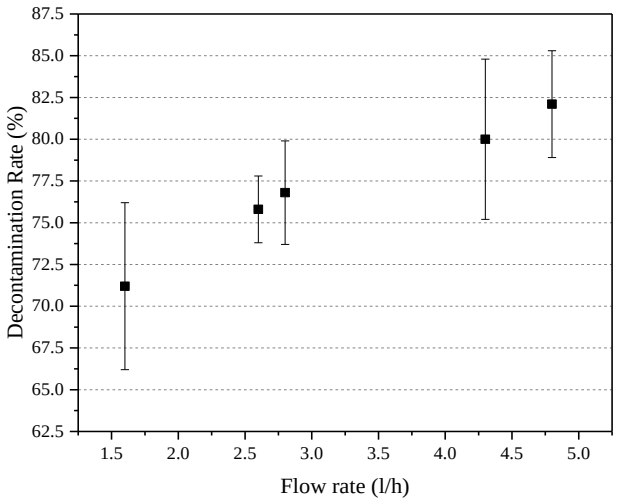

Fig. 5.21 Effect of flow rate on the decontamination rate of SC-CO_2 cleaning

5.3.7 Effect of Co-solvent

Supercritical carbon dioxide has been widely used in extracting particular compounds from medical plants, coffee beans etc. However, the efficiency was usually low for pure CO_2 in extracting target compounds from a sample (Yang et al., 1995), due to the low polarity of CO_2 molecules. Consequently, co-solvents that could modify properties of the SCF were always used to promote the efficiency of the process (Hawthorne, 1990). A co-solvent in an SCF system could either increase the solubility of the target compounds in the fluid or interact with active sites within the extraction samples, resulting in an increment in the efficiency or yield in a extraction process (Tonthubthimthong et al., 2004).

Researchers have used many polar or non-polar organic substances, in different mole fractions, as co-solvents to study extracting target compounds by use of supercritical CO_2, which comprised methanol, ethanol, acetone, etc. (Cao et al., 2005, Sánchez-Vicente et al., 2009, Huang et al., 2004). Cleaning by use of supercritical CO_2 was intrinsically an extraction process, as well. To investigate the effect of co-solvents in enhancing the efficiency of SCF cleaning, ethanol, acetone and ethyl acetate were selected as co-solvents in the test because they were with different polarities from that of CO_2 and were relatively safe in the experiment procedures.

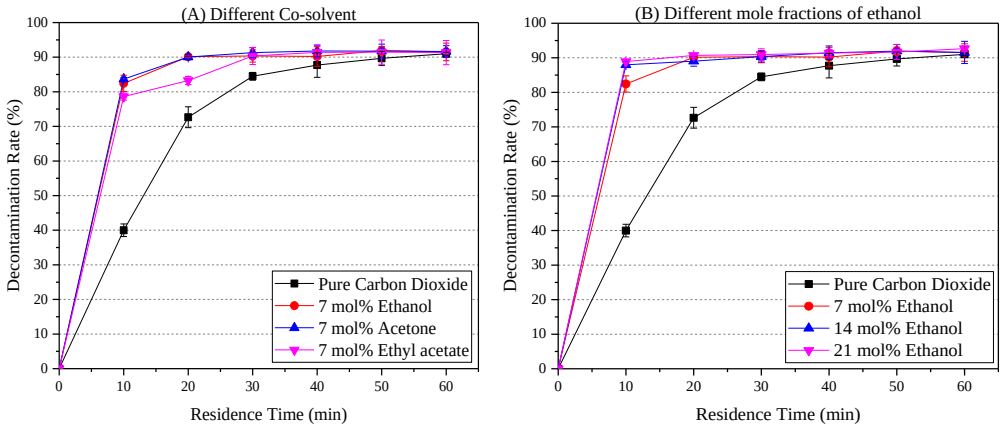

Fig. 5.22 Decontamination rate curves against residence time with different co-solvent additions (A) and at different concentrations (B)

Fig. 5.22 (A) is the comparison of decontamination curves between pure CO_2 and additions of 7 mol% co-solvents into the SCF system; other parameters were controlled within the identical values as that in the above sections. The cleaning efficiency of supercritical system was dramatically increased when co-solvents were introduced into the system, with only 10 minutes being required to reach 80% of the decontamination rate. By contrast, it needed 30 minutes to remove more

than 80% contaminants from samples. Maximal decontamination rates could be reached in 30 minutes with the addition of co-solvents, demonstrating there were interactions between molecules of co-solvents and contaminants. Co-solvents in this test were polar materials, modifying the properties of the SCF, which had low solubility for inorganic and organic substances with strong polarity. Co-solvent molecules could introduce stronger van der Waals forces and specific molecular interactions into the system, which could more effectively drag extractable molecules from contamination layers. Acetone and ethanol had similar enhancement in the decontamination rate, being slightly higher than the ethyl acetate. From the safety and economic perspectives, ethanol was used as the co-solvent to modify SC-CO_2 properties and increase the cleaning efficiency in oil contamination cleaning.

Fig. 5.22 (B) shows the decontamination rate changes with various concentrations of ethanol as a co-solvent in the SC-CO_2 cleaning system. As can be seen, the higher concentration of ethanol was in the cleaning vessel, the less time was required in the cleaning operation. Similarly, the conclusions from Fig. 5.22 (A), however, the higher concentration could not increase the eventual decontamination rate in oil cleaning. 21 and 14 mol% fractions in the SC-CO_2 system generated similar enhancement, at slightly higher than 7 mol% fractions, with only about 5% increment in the initial ten minutes. After 20 min cleaning duration, three different co-solvent concentrations produced a similar result of 90% decontamination rates. Consequently, 7 mol% of ethanol in the SC-CO2 cleaning system would be adequate for optimising the cleaning process.

5.4 DoE Study for SC-CO_2 Cleaning

The object selected in this study was the same as the previous section, using motor oil HPO TURBO SG/CF-4 5W30. For the convenience of installation, the absorbent pads were 4 cm × 4 cm, soiled with lubricating motor oils. CO_2 had 99% purity and the co-solvents were dehydrated ethanol 99%.

5.4.1 Experimental Design and Statistical Analysis

Table 5.3 Factors and levels in cleaning experiments

Parameters	Units	Symbol	Alias	Levels	
				Lower	Upper
Temperature	°C	T	A	65	75
Pressure	MPa	P	B	22	25
Time	min	τ	C	30	40
Flow rate	l/h	Q	D	4.8	6.8
Co-solvent	-	E	E	No	Ethanol

In preliminary studies, all factors affecting the cleaning performance such as operating temperature, pressure, cleaning time, SC-CO_2 solvent flow rate, and co-solvent were studied. A design of experiments determined the most significant factors that might affect the cleaning performance and optimise the cleaning process. In this section, the cleaning performance index (*CPI*) was calculated based on Eq. (5.2), as well as the previous Chapter. To generate the relationship between the *CPI* and the five process variables, fractional factorial design was employed to investigate the response in terms of temperature (T), pressure (P), cleaning time (τ), CO_2 flow rate (Q), and co-solvent. A two-level, five factors, half-fraction factorial design approach was applied, which means each factor was studied at both low and high levels. The responses were expressed in terms of *CPI*.

Independent variables and their respective levels in cleaning experiments are listed in Table 5.3. In a half-fraction factorial design, the number of centre points per block was set as three.

A second-order polynomial model, as shown in Eq. (5.3), was used to express the *CPI* as a function of the independent variables. Minitab (V17.3.1, Minitab, USA) statistical software was used to create and analyse the experimental data so that the effect of various factors on SC-CO_2 cleaning performance could be determined. The DoE guarantees orthogonality of the experiment and avoid confounded effects of crucial parameters in the experiment. The halved experiment was generated based on a 2_{V}^{5-1} experiment design with the defining relation of I=ABCDE, as shown in Table 5.4. The subscript V was the resolution of this design, demonstrating that the main effects only confounded with the fourth order sections, which were apparently insignificant factors in this study. Superscript '5-1' meant the partial factorial experiment was half implemented based on a full five-factor experiment. The accuracy of the fit to the regression model is represented by the determination coefficient (R^2), whilst analysis of variance (ANOVA) was used to evaluate the statistical significance of the model, considering regression values and the root mean square of residual error. The test of statistical significance was based on the total error criteria within a confidence level of 95%.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 \sum_{i-1}^{k-1} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{5.3}$$

In this model, y is the response caused by parameter variations, β_0, β_i, β_{ii} and β_{ij} are constant regression coefficients of the model, x_i and x_j are the levels of the

independent variables and ε is the error associated with the model.

Table 5.4 The arrangement of the halved experiment

A	B	C	D	E	A ×B	…	D ×E	…	A ×B ×C ×D ×E
1	1	1	-1	-1	1	…	1	…	1
1	-1	1	1	-1	-1	…	-1	…	1
1	-1	-1	1	1	-1	…	1	…	1
1	1	-1	-1	1	1	…	-1	…	1
-1	-1	-1	1	-1	1	…	-1	…	1
1	1	-1	1	-1	1	…	-1	…	1
-1	1	-1	1	1	-1	…	1	…	1
-1	1	1	1	-1	-1	…	-1	…	1
1	-1	1	-1	1	-1	…	-1	…	1
1	1	1	1	1	1	…	1	…	1
-1	1	1	-1	1	-1	…	-1	…	1
-1	1	-1	-1	-1	-1	…	1	…	1
-1	-1	1	-1	-1	1	…	1	…	1
1	-1	-1	-1	-1	-1	…	1	…	1
-1	-1	-1	-1	1	1	…	-1	…	1
-1	-1	1	1	1	1	…	1	…	1

5.4.2 Visualisation of the experiment results

The response for all experimental runs in terms of the independent parameters are shown in Table 5.5. A regression analysis was also conducted for the experimental data using a least squares approach. The ANOVA has been summarised in Table 5.6.

Table 5.5 Experimental design conditions and corresponding results

Run	Temperature (℃)	Pressure (MPa)	Cleaning time (min)	Flow rate (l/h)	Co-solvent	CPI (%)
1	75	25.0	40	4.8	No	87.6472
2	70	23.5	35	5.8	No	84.4723
3	75	22.0	40	6.8	No	87.5285
4	75	22.0	30	6.8	Ethanol	87.6650
5	70	23.5	35	5.8	No	86.1529
6	75	25.0	30	4.8	Ethanol	87.6577
7	70	23.5	35	5.8	Ethanol	86.8665
8	65	22.0	30	6.8	No	80.6577
9	75	25.0	30	6.8	No	86.4723
10	65	25.0	30	6.8	Ethanol	86.1529
11	65	25.0	40	6.8	No	83.3153
12	75	22.0	40	4.8	Ethanol	88.5285
13	75	25.0	40	6.8	Ethanol	90.4723
14	65	25.0	40	4.8	Ethanol	87.6472
15	65	25.0	30	4.8	No	81.9388
16	65	22.0	40	4.8	No	80.1529
17	70	23.5	35	5.8	Ethanol	86.5777
18	70	23.5	35	5.8	No	86.1577
19	75	22.0	30	4.8	No	86.6647
20	70	23.5	35	5.8	Ethanol	86.7666
21	65	22.0	30	4.8	Ethanol	83.1529
22	65	22.0	40	6.8	Ethanol	83.1529

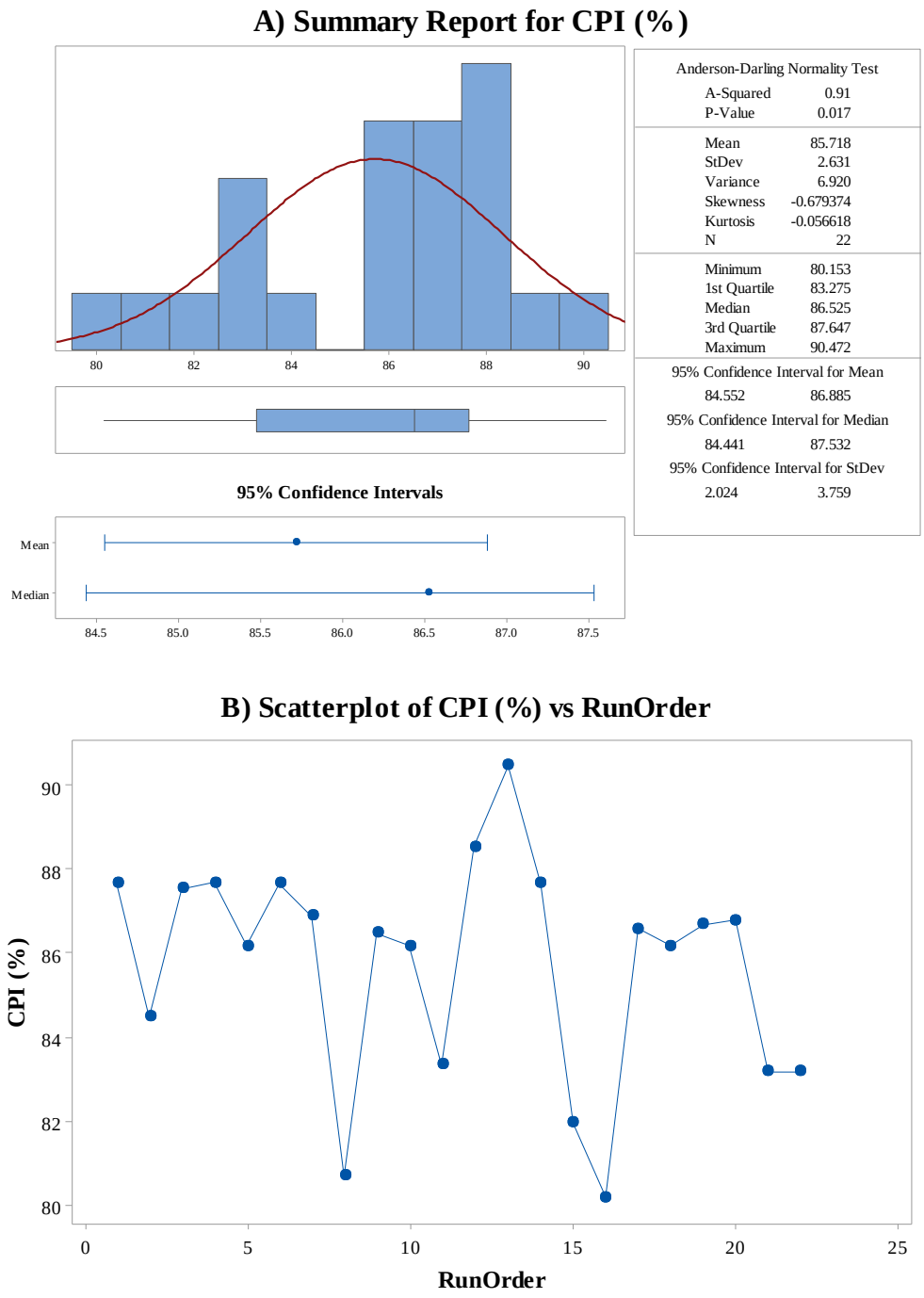

Fig. 5.23 The graphical summary and visualisation of experiment data

Fig. 5.23 was plotted based on the experiment data in the Table 5.5. From chart A, it can be concluded that there was no singularity in the data. The scatter of *CPI*

versus run orders in chart B demonstrates a normal trend within the experiment data; no apparent declining or inclining trend are observed.

5.4.3 Fitting Models

Using the Analyze Factorial Design module in Minitab 17, the Pareto chart of standardised effects were obtained, along with the ANOVA of experiment data. Pareto analysis is the technique used for decision making based on the Pareto Principle, known as the "80 – 20" rule for data analysis. It is such a technique that statistically separates a limited number of input factors having the greatest impact on an outcome, either desirable or undesirable. The numbers 80 and 20 are not meant to be absolute but a great majority of problems (80%) are produced by a few key causes (20%). That means if the few key causes can be rectified, then a better probability of success will be achieved. A Pareto plot visually represents the absolute values (*t*-value in Table 5.6) of the effects of the main factors as well as the effects of the interaction of different factors. A reference line is drawn to indicate that the factors which extend past this line are potentially important (Moore and Mccabe, 2005). The most important factor is represented by the tallest bar; the next important problem is represented by next tallest bar, and so on (Antony, 2014). It can be seen from Fig. 5.24 that temperature had the greatest effect on the removal of motor oil, followed by co-solvent and pressure. The effects that are above the reference line are statistically significant at 95% confidence level. The relative importance of each factor and combination of factors can be observed from the Pareto plot. The normal plot of the standardised effects in Fig. 5.25 also demonstrated that the temperature, pressure, their interactions and co-solvents were significant factors in this experiment.

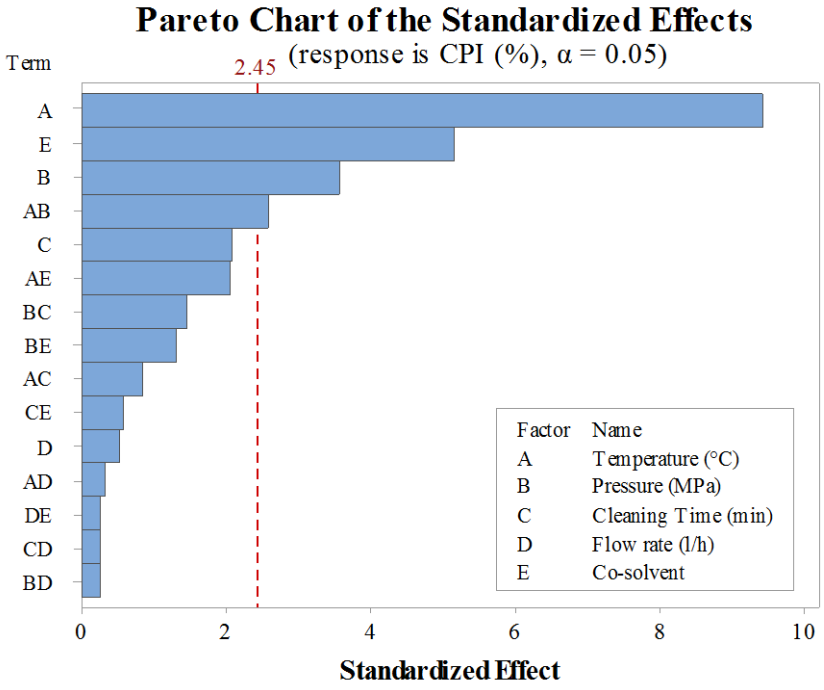

Fig. 5.24 Pareto chart of the standardised effects

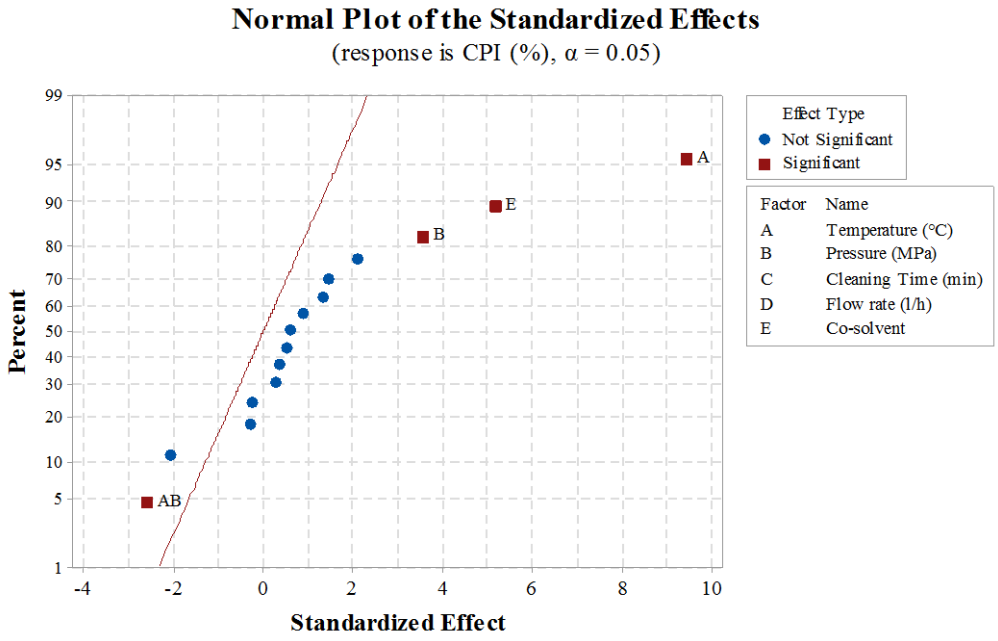

Fig. 5.25 Normal plot of standardised effects for CPI

Table 5.6 Analysis of variance (encoded) for the experiment in Table 5.5

Source	**DF**	**Adj SS**	**Adj MS**	***F*-Value**	***P*-Value**
Model	15	139.703	9.3135	9.96	0.005
Linear	5	124.412	24.8823	26.6	0.001
Temperature (A)	1	83.109	83.1087	88.85	**0**
Pressure (B)	1	11.904	11.9035	12.73	**0.012**
Cleaning Time (C)	1	4.083	4.0832	4.37	0.082
Flow rate (D)	1	0.257	0.2568	0.27	0.619
Co-solvent (E)	1	25.059	25.0594	26.79	**0.002**
2-Way Interactions	10	15.291	1.5291	1.63	0.283
A ×B	1	6.344	6.3441	6.78	**0.04**
A ×C	1	0.702	0.7017	0.75	0.42
A ×D	1	0.098	0.0981	0.1	0.757
A ×E	1	4.03	4.0305	4.31	0.083
B ×C	1	1.987	1.9865	2.12	0.195
B ×D	1	0.065	0.0646	0.07	0.801
B ×E	1	1.601	1.6009	1.71	0.239
C ×D	1	0.068	0.0677	0.07	0.797
C ×E	1	0.32	0.3198	0.34	0.58
D ×E	1	0.077	0.0775	0.08	0.783
Error	6	5.612	0.9353	/	/
Curvature	1	1.651	1.6515	2.08	0.208
Lack-of-Fit	1	2.029	2.0292	4.2	0.11
Pure Error	4	1.931	0.4828	/	/
Total	21	145.315	/	/	/
S = 0.967132 R-sq = 96.14% R-sq(adj) = 86.48% R-sq (pred) =0.00%					

It can be apparently seen from Table 5.6 that the *P*-value for the model term was 0.005, significantly less than the significance level of α=0.05, demonstrating that the overall effect of the selected model was significant and valid. The *P*-value for the curvature term was 0.208; therefore, no apparent curvature trend existed in the selected model. In the lack-of-fit row, the *P*-value was 0.11, meaning the fitting of the model did not have apparent lack-of-fit conditions.

5.4.4 Model Simplification and Residual Diagnosis

The above analysis through Pareto Chart and ANOVA demonstrated that the terms of temperature, pressure, their interactions and co-solvent were significant factors in the test range of the experiment. Accordingly, the simplification stage selected only the four terms with significant effects on the regression model, along with the six centre points.

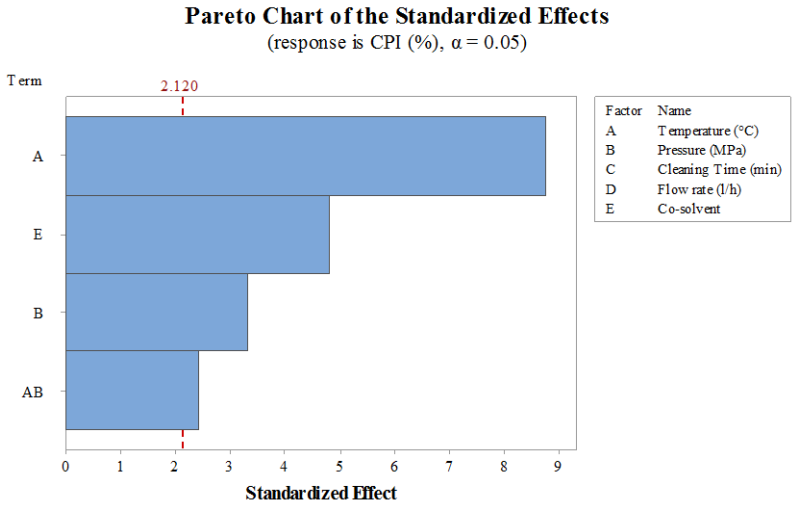

Fig. 5.26 Pareto chart of standardised effects after simplification

From the Pareto chart in Fig. 5.26 and corresponding normal plot in Fig. 5.27, it can be concluded the selected factors, under the condition of significance level α=0.05, were feasible and adequate to establish a model describing the relationship between *CPI* and the vital factors. The estimate effects and coefficients for *CPI* in Table 5.8 is the result of significant factors and their respective interactions. Combining the estimates and ANOVA in Table 5.7, the remaining factors were all with P-value less than the significance level, demonstrating that they were all significant in the regression model. The *P*-value of the remaining 2-way

interaction A×B was 0.027, less than the significance level 0.05. Consequently, it was also a significant factor in the regression model.

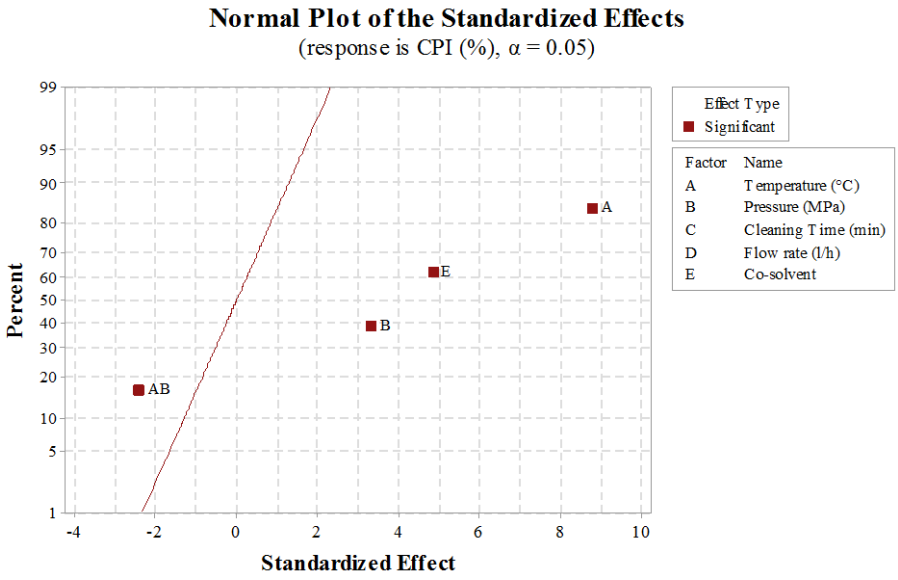

Fig. 5.27 Normal plot of standardised effects for CPI after simplification

Table 5.7 Analysis of variance (encoded) for the experiment after simplification

Source	**DF**	**Adj SS**	**Adj MS**	***F*-Value**	***P*-Value**
Model	5	128.067	25.6134	23.76	0
Linear	3	120.072	40.0239	37.13	0
Temperature (A)	1	83.109	83.1087	77.1	0
Pressure (B)	1	11.904	11.9035	11.04	0.004
Co-solvent (E)	1	25.059	25.0594	23.25	0
2-Way Interactions	1	6.344	6.3441	5.89	0.027
A×B	1	6.344	6.3441	5.89	0.027
Error	1	1.651	1.6515	1.53	0.234
Curvature	16	17.248	1.078	/	/
Lack-of-Fit	12	15.317	1.2764	2.64	0.18
Pure Error	4	1.931	0.4828	/	/
Total	21	145.315	/	/	/
S = 1.03827 R-sq = 88.13% R-sq(adj) = 84.42% R-sq (pred) = 77.03%					

Table 5.8 Estimate effects and coefficients for CPI (Encoded)

Term	Effect	Coef	SE Coef	*t*-Value	P-Value	VIF
Constant	85.55	0.26	329.59	0	/	
Temperature (A)	4.558	2.279	0.26	8.78	0	1
Pressure (B)	1.725	0.863	0.26	3.32	0.004	1
Co-solvent (E)	2.135	1.067	0.221	4.82	0	1
A ×B	-1.259	-0.63	0.26	-2.43	0.027	1
Centre Point	/	0.615	0.497	1.24	0.234	1

5.4.5 Residual Diagnosis

It is not rigorous to assess the fitting model simply based on the ANOVA and the estimate effects and coefficients. The objective of this step is to evaluate the feasibility of the fitting model from the perspective of residuals, which would be normal if the fitting model and the experiment data are normal. Fig. 5.28 gives a four-in-one graph of residuals that were plotted in different forms. The normal probability plot and corresponding histogram for residuals has been demonstrated in Fig. 5.28 A) and C), respectively. The *P*-value obtained from the normality test was 0.761; residuals can be accordingly considered as subjecting to normal distribution. The scatter in Fig. 5.28 B) illustrates the residuals versus fitted values of the response variables. The analysis surrounding this plot main focuses on assessing the integrity of sum of square and the shape of the scatter. No funnel- or speaker-shaped distribution of the residuals were observed in the scatter; it is accordingly concluded that the scatter was in the normal condition. Along with the four scatters in Fig. 5.29, it can be concluded that no curvature trend existed in this test. In the chart of residuals versus observation orders (Fig. 5.28 D), residuals for different observation orders fluctuated randomly around the horizontal line, without inclination or declining trend, demonstrating the data obtained from

experiment were at a normal level.

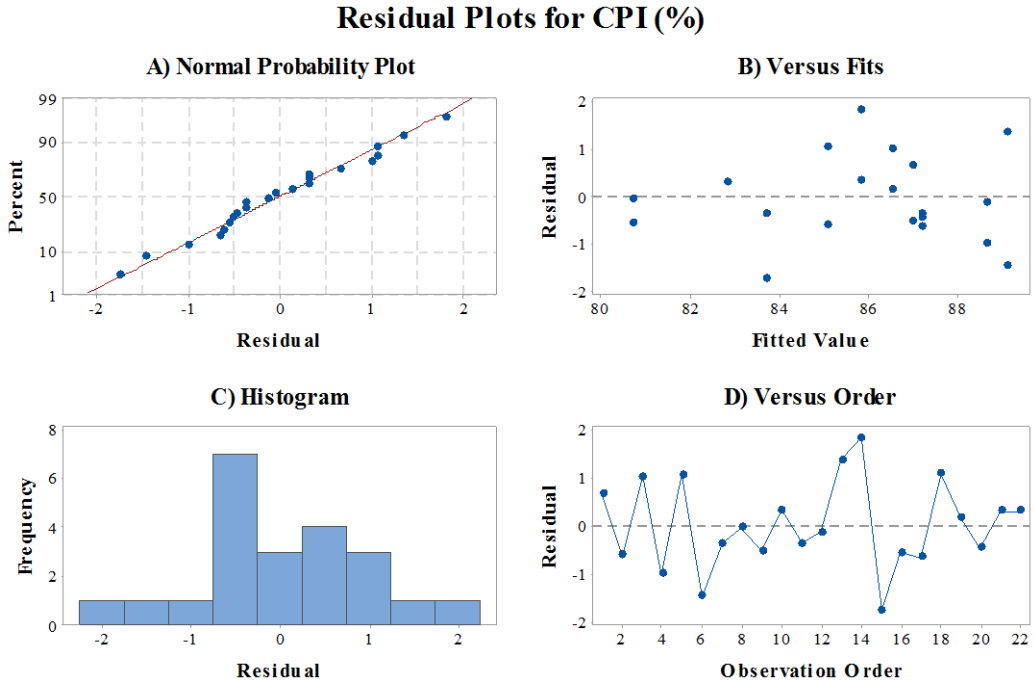

Fig. 5.28 Four-in-one graph of residual for CPI

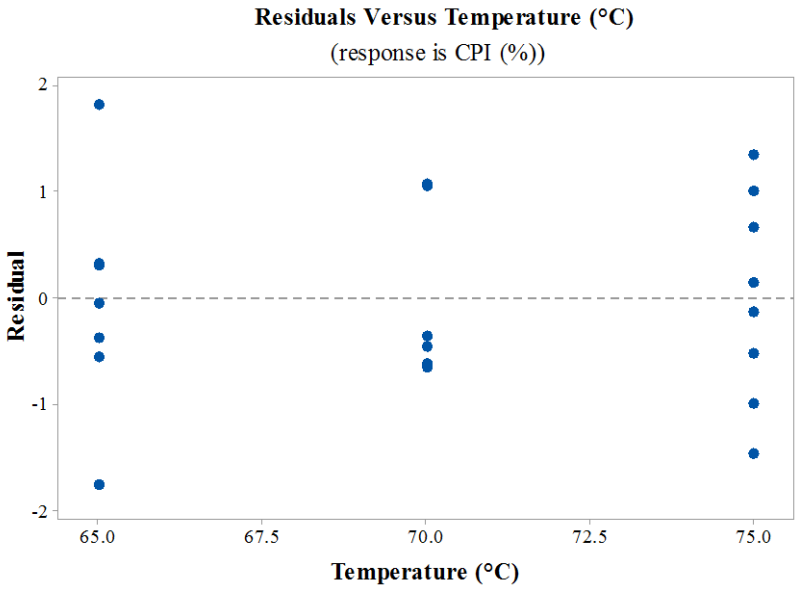

Fig. 5.29 Residual scatters against temperature

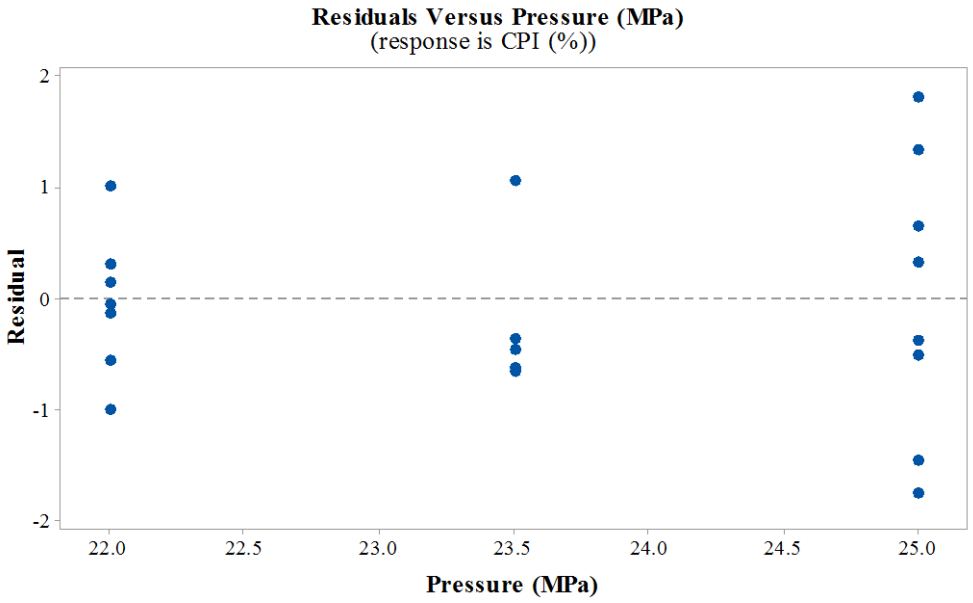

Fig. 5.30 Residual scatters against Pressure

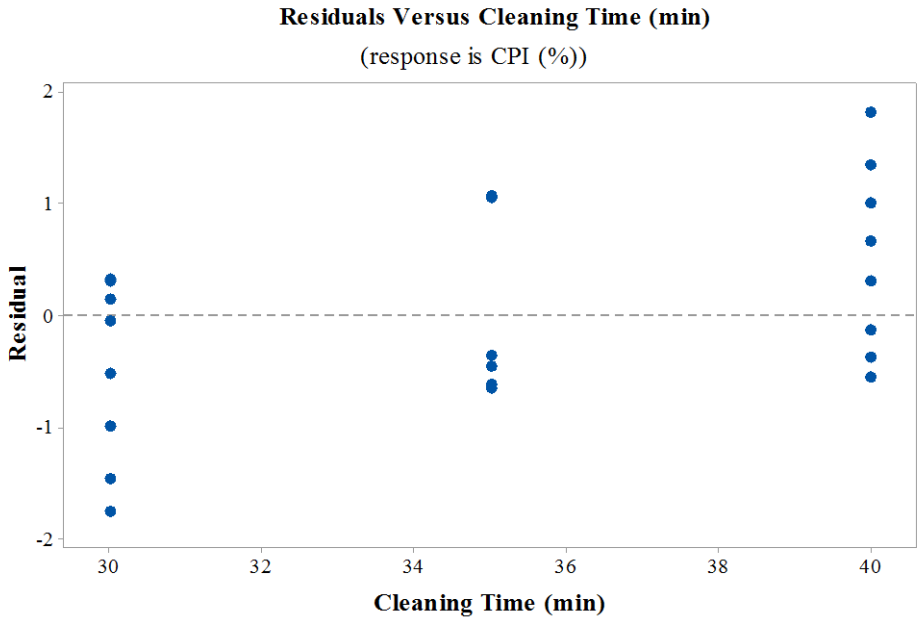

Fig. 5.31 Residual scatters against cleaning time

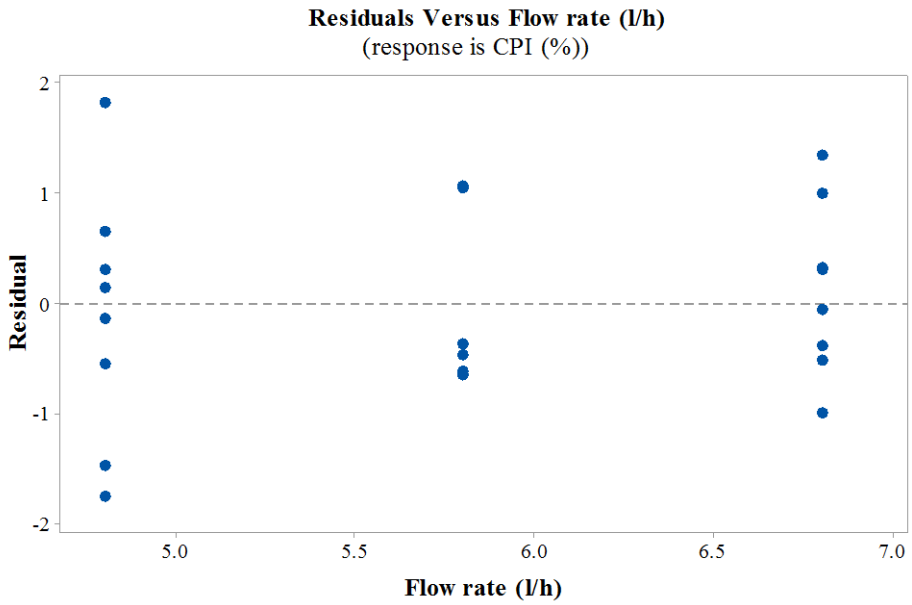

Fig. 5.32 Residual scatters against flow rate

5.4.6 Model Interpretation

The design of experiments was used to determine the most significant factors that might affect the cleaning performance and to optimise the operating conditions. The experimental results were used to determine the parameters of a second-order polynomial model in Eq. (5.3) by employing the least squares technique. The model presents the relationship between the CPI and process variables. Using the experimentally measured results in Minitab 17 statistical software, the process variables that were not significant were eliminated, and the final model was refitted. The refined predicted model is

$$CPI = -97.8 + 2.429T + 6.45P + 1.067E - 0.0840T \times P \qquad (5.4)$$

where CPI denotes the cleaning performance index, T denotes operating

temperature, °C, P denotes the operating pressure, MPa and $E \in \{0,1\}$.

Eq. (5.4) is an empirical model used to estimate the response of CPI for motor oil removal by SC-CO_2 from the independent variables within the experimental range. From the ANOVA analysis summarised in Table 5.7, the difference between the R^2 value (88.13%) and the adjusted R^2 value (84.42%) was extremely small and the P-value for lack of fit (0.104) was much greater than 0.05. Furthermore, residual plots, which are used to determine if the ordinary least squares assumptions are satisfactory to produce unbiased coefficient estimates with minimum variance, were used to examine the goodness of a fit in regression analysis and ANOVA. One of the key assumptions for the statistical analysis is that all of the data come from a normal distribution. Fig. 5.28 C) shows the normal probability plot (residual) for the *CPI* of SC-CO_2 cleaning. It is clear that all the points are fairly close to the straight line. Therefore, the experimental data satisfy a normally distributed population, indicating that the model adequately represents the real relationship among the process variables.

The main effect is an outcome that can show the consistent difference between levels of a factor. Fig. 5.33 shows the main effect for motor oil removal by SC-CO_2, illustrating the relative strength of effects of various factors. The sign of the main effect indicates the directions of the effect. It can be seen that the effect of temperature was characterised by a greater degree of departure from the overall mean. Temperature, pressure and co-solvent had a positive effect on the removal of the motor oil, while the other two factors, cleaning time and CO_2 flow rate showed a slight positive effect on the removal.

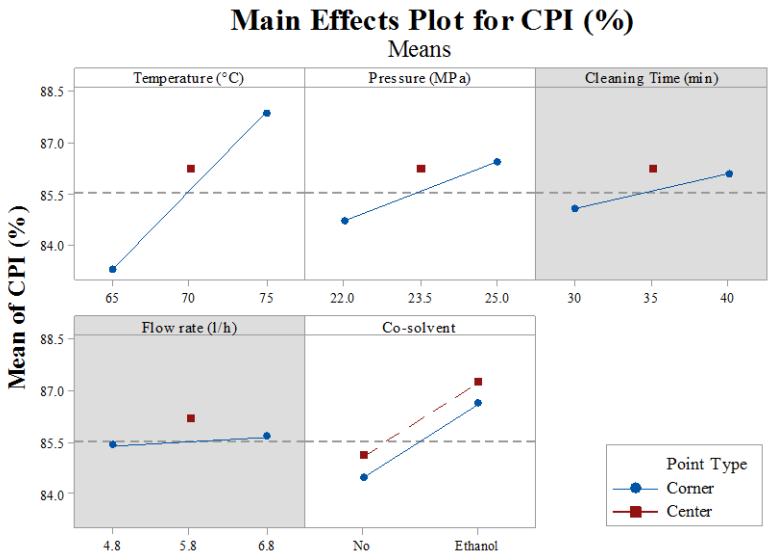

Fig. 5.33 Main effects plot for temperature, pressure, cleaning time, flow rate and co-solvent for CPI in SC-CO_2 cleaning.

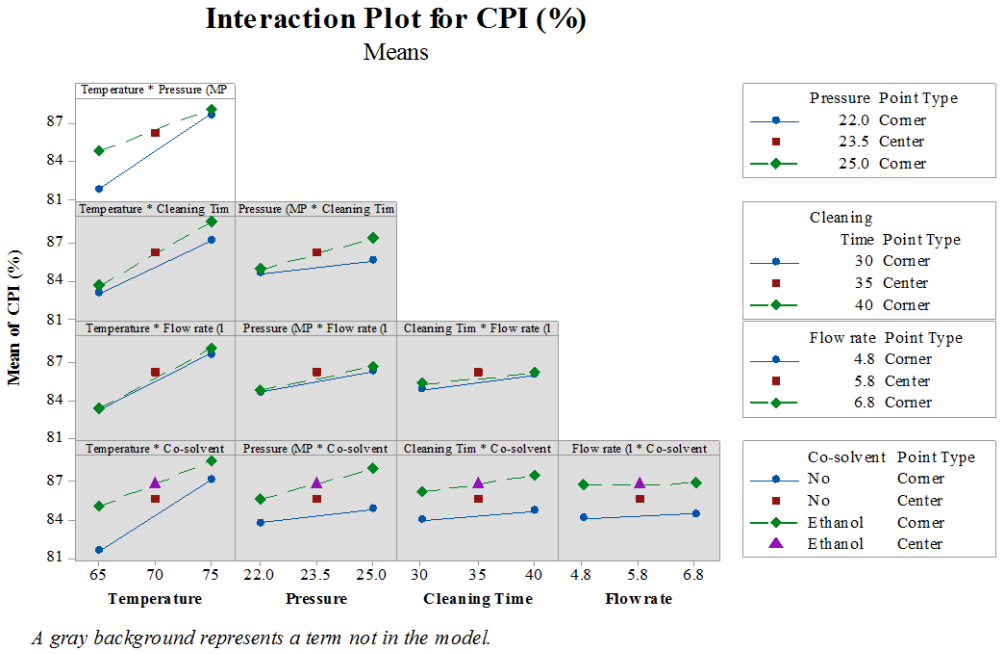

Fig. 5.34 Interaction effects plot for temperature, pressure, cleaning time, flow rate and co-solvent for CPI in SC-CO_2 cleaning

The interaction effect plot is shown in Fig. 5.34 for motor oil removal by SC-CO_2. The plot provides the main response to two factors at all possible combinations of their settings. If the lines are not parallel, it is an indication that the two factors interact with each other (Antony, 2003). As shown in Fig. 5.34, the temperature interacts strongly with pressure, whereas other interactions showed less prominent features. It was possible that temperature and pressure may influence the mass transfer properties of the components and reaction (Ciftci and Temelli, 2011). In this experiment, the CPI increased with increasing temperature and pressure, as can be seen in Fig. 5.34. Similar results were also found by other research (Della Porta et al., 2006, Danh et al., 2012). During the process of removing dried inks and adhesive residues from the microscopic cells of engraved rollers, the temperature was increased from 40 ℃ to 100 ℃, with the pressure being maintained constantly at 150 bar, in order to improve the removal of the stained oil from degreasing metal parts (Della Porta et al., 2006). As shown in Fig. 5.34, it was found the solubility increased with the pressure due to a subsequent increase of the solvent density; however, the effect of temperature was not as straightforward. For the influence of temperature on solubility, there were two major phenomena. The increase in temperature decreased the density of the solvent by negatively affecting the extraction, while it had improved the solute volatility which was positive to *CPI*. However, when the pressure lowered near to the critical point, the effect of solvent density was dominant compared with that of volatility, and therefore a rise in temperature resulted in a reduction in CO_2 density and a consequent decrease in solute solubility, whereas if the pressure was high, the effect of the density's reduction did not exceed the effect of increasing in the solute solubility (Danh et al., 2012).

5.4.7 Optimisation of Cleaning Conditions

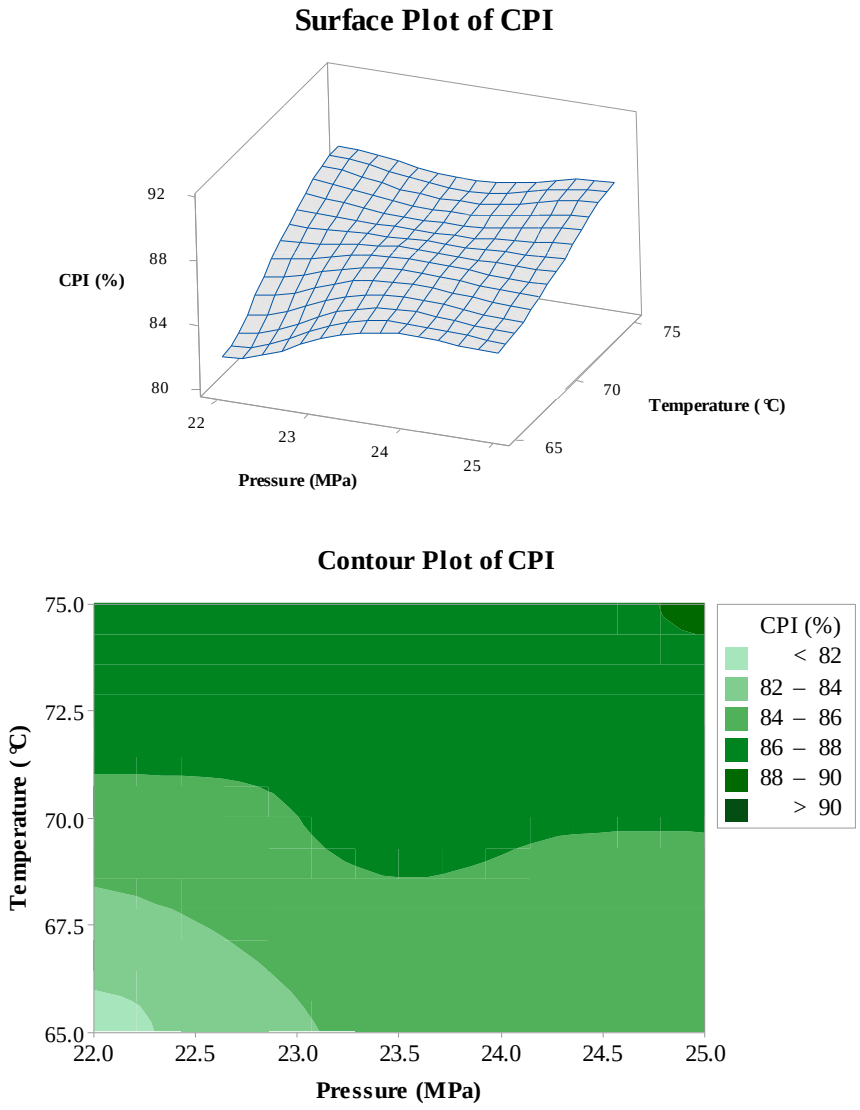

Fig. 5.35 CPI surface and contour plots as a function of temperature and pressure in SC-CO_2 cleaning

SC-CO_2 cleaning conditions could be optimised to give the maximum *CPI* using the numerical optimisation feature of Minitab software. Based on Eq. (5.4), the highest *CPI* was estimated to be 89.30% was obtained at 25.0 MPa, 75 °C and

with ethanol as co-solvent. Fig. 5.35 was a 3-D plot and a contour for temperature-pressure *CPI*. They showed the effects of the two significant parameters, pressure and temperature, on the *CPI*. It is clear that the *CPI* was significantly affected by pressure variations. At a constant temperature, the *CPI* increased with pressure to a certain value which also agreed with the experimental results. Similar results were found in removal of lubricating oils from metallic contacts using SC-CO_2 (Viguera et al., 2013), where the higher temperature benefited the removal of the lubricating oils from metallic contacts when the cleaning was operated at a high pressure.

5.5 Summary and Conclusions

Greasy contaminant and carbon depositions exist in the internal of decommissioned engines. Carbon depositions can be found on the nozzles, pistons, valves and heat shields while the distribution of greasy contaminants is more extensively, e.g. on the rocker arms, tapper and nuts. These carbon depositions were due to the incomplete combustion of the fuels, transported by the inhalation and exhaust emission, and adhered to the neck of the valve by a very strong adhesive force. In this chapter, the contaminants from decommissioned engines were analysed using a series of detection and analysis tools, such as microscopic observation, Fourier Transform infrared spectroscopy analysis, energy dispersive spectrometer. Carbon and hydrogen are the major elements in contaminants, which accounts for more than 40% by weight. The FTIR spectroscopy of the carbon deposition, oil contaminants and lubrication oil illustrates the broad existence of saturated hydrocarbon bonds $(–CH_2–)_n$ in the contaminants, suggesting the

feasibility of SC-CO_2 with respect to diesel engine cleaning. EDS and EPMA methods also detected the existence of other elements e.g. Phosphorus, Sulphur, Aluminium and Zinc in the contaminants, which originated from the additives in the lubricating oil and the abrasion debris of the engine parts. Based on the contaminant composition and elemental analysis, it could be concluded that the SC-CO_2 would be a feasible approach to the cleaning of oily compositions in the contaminants of engines as a green alternative of the organic solvent.

The impacts of SC-CO_2 cleaning on greasy and oily contaminants were evaluated by use of lubricating oils and greases as the study targets. Pilot experiments have been carried out for the qualitative and quantitative studies of SC-CO_2 cleaning by use of the lubricating greases. The maximum removal rate could reach approximately 43% after cleaned in SC-CO_2 for 2.5 hours and the optimal cleaning results were obtained at pressure and temperature of 20 MPa and 70°C, respectively. However, the results showed that large quantities of substances remained on the metallic patches and turned into solidified scales with opaque appearances. It could demonstrate that there had been internal structural changes in the greases and the residual scales required additional operations for thorough cleaning.

Because the oily compounds accounted for the major proportion in engine contaminants, more specific studies were carried out using lubricating oils as the contaminant samples in this chapter. Five crucial parameters were investigated and their respective performances were evaluated using the single factorial experiments on the 100 mm × 100 mm × 2 mm oil absorbing pads. In the test range, the decontamination rate could attain as high as over 90%, which was significantly

greater than that of grease cleaning. The pressure had positive impacts on the decontamination rate in the test range; the higher the cleaning pressure was, the greater cleaning capacity SC-CO_2 had in a fixed duration. However, impacts of temperature on the cleaning efficiency were more complicated. At a lower pressure range, the temperature presented a negative impact, but it turned positive at a higher pressure. The competition effect from the temperature and pressure was especially obvious at pressure from 10 MPa to 22 MPa, where a peak could be observed in the decontamination rate line chart. Therefore, the optimal temperature and pressure were determined to be between 55 – 75 °C and 20 – 30 MPa. The decontamination rate changed very little when cleaned after 40 min in the system; consequently, 30 – 40 minutes would be adequate to attain an ideal cleanliness. Increasing the flow rate in the system could promote the dissolution of contaminants into SCF; however, the increment was extremely low. Therefore, the flow rate for SC-CO_2 cleaning was selected to be between 4 – 5 l/h. With the addition of co-solvents, the cleaning time was significantly reduced, but the effects from different mole fractions of co-solvents in the supercritical system were not as significant in this study. From safety and economy perspectives, 7 mol% ethanol additions are adequate in the SC-CO_2 cleaning.

A mathematical model was established using the 2_V^{5-1} partial factorial experiment design for the further study of parameters in SC-CO_2 cleaning. Results showed that the temperature, pressure, their 2-way interaction and the co-solvent were the significant factors affecting the cleaning performance index. The model is sufficient to predict accurately the cleaning performance index, which is largely influenced by process parameters including temperature, pressure, cleaning time,

flow rate of CO_2 and co-solvent. The effect of SC-CO_2 on the cleaning performance was analysed, to characterise and optimise the SC-CO_2 cleaning process in the tested range. The successful experimental results showed that the *CPI* (cleaning performance index) increased at higher temperature, higher pressure with dehydrated ethanol as co-solvent, and the optimal cleaning performance, calculated to be 89.30%, was obtained at 25.0 MPa, 75 °C. The optimum process parameters are highly recommended for processing heavily contaminated metallic engine components.

The only disadvantage of supercritical cleaning is the high pressure used in the cleaning vessel. Normally, equipment designed for elevated pressure is more expensive than that required for conventional chemical solvents employed at atmospheric pressure. Based on the results presented in this Chapter, SC-CO_2 cleaning is an effective means for the remanufacturing cleaning process for automobile engines with easy solvent recovery.

Chapter 6

SC-CO_2 Combined with Liquid Blasting

Based on the study from Chapter 5, the feasibility of SC-CO_2 has been confirmed as an alternative solvent in cleaning operation though results indicated that subsequent removal operations are still required to obtain a satisfactory cleanliness. The actual polluting conditions on engine parts can be more complicated with a higher proportion of insoluble compounds than in lubricating oils. This chapter proposes a new cleaning technology combining two cleaning methods: the SC-CO_2 cleaning as the pre-treatment and liquid blasting as the successive treatment to remove the residues thoroughly from decommissioned engines.

6.1 The Morphology Changes of Contaminants

A cleaning process can be considered to be equivalent to a chemical reaction, with the dissolution of deposits of mineral or inorganic salt (Wolkoff et al., 1998) and also their physical removal by vibration, cavitation or frictional effects (Awad and Nagarajan, 2010, Shi et al., 2014, Vasiljev et al., 2013). In cleaning by use of SC-CO_2, the CO_2 fluid corrodes the contaminants primarily by dissolving their soluble compounds and generating pores and cracks that change the structure of contaminants and strips off micro debris from the contaminant layer. Among all the effects that CO_2 fluid exerted on the contaminants, the mass transfer was the

predominant.

Dissolution: The SC-CO_2 possesses extraordinary properties as a solvent, such as the high solubility for organic compounds, relatively low surface tension, low viscosity and high diffusion coefficients. Therefore, a SC-CO_2 fluid could dissolve and remove non-polar and low polarity substances that are in a small molecular weight including hydrocarbons, esters, alcohols and even some solid substances. As for a retired engine, the contaminants mostly comprised lubricating oils, greases, fuels, their degradation products and carbon depositions. Carbon dioxide molecules could penetrate the contamination layer, dissolve the target molecules and remove them into the fluid streams, leaving pores and cracks within the contamination structures. From the previous chapter, the cleaning efficiency could be controlled by adjusting parameters such as the temperature, pressure and co-solvents to attain an optimal cleaning result.

Erosion: In the cleaning vessel, the supercritical fluid was in a flowing state. The shear forces, generated at the interface between fluids and contaminants, scrubbed the contaminants off the substrates and thus improving the cleaning efficiency. The flow rate, among all the parameters, had a significant impact on the scrubbing effects from the fluids; conventionally, the higher the flow rate is, the greater shear forces are.

Foaming: Carbon dioxide molecules could penetrate through the interface into contaminants and form a miscible mixture with the oily compositions at a high pressure. Once the pressure rapidly dropped, CO_2 molecules that originally dissolved in the contaminants precipitated and converged into micro bubbles

inside the contaminant layers. These bubbles gradually became larger as a result of pressure drops and increasing CO_2 precipitations, destroying the original structures of contaminants and forming pores and cracks.

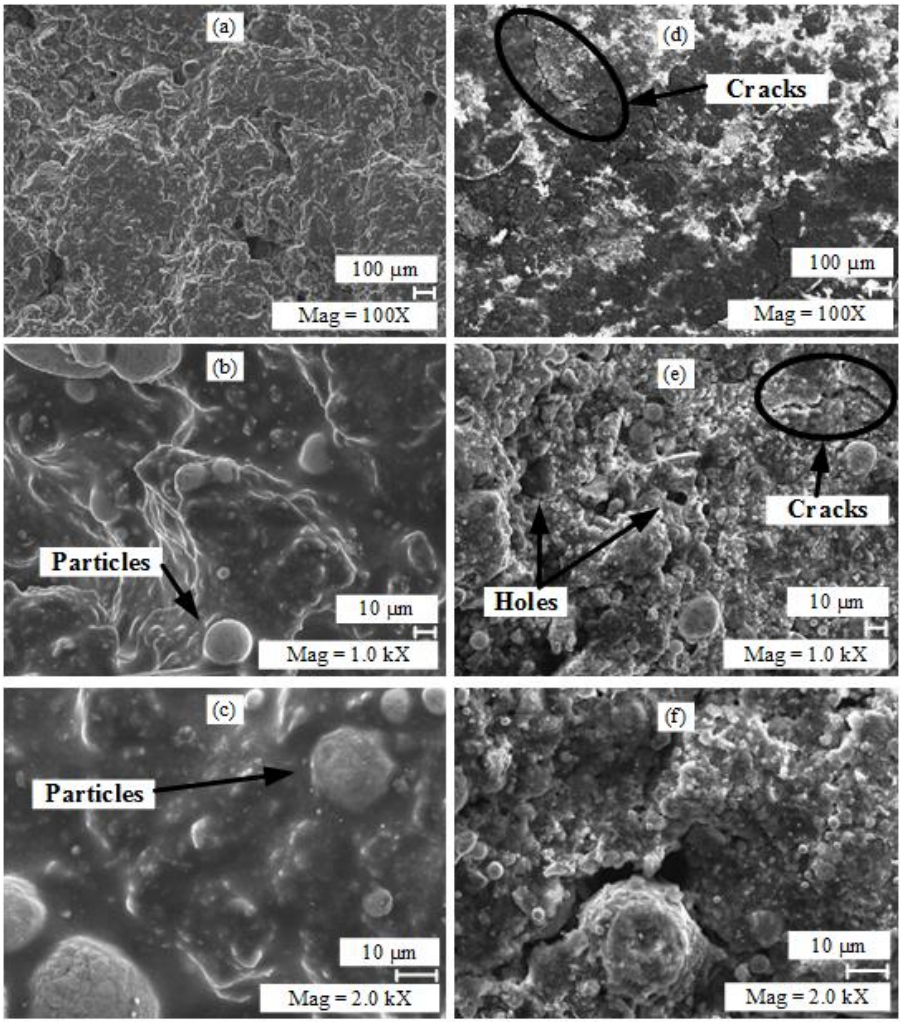

Fig. 6.1 Microscopic view of contaminant on real objects before (a, b, c) and after (d, e, f) the SC-CO_2 cleaning

The retired engine parts were cleaned in the SC-CO_2 using the optimal parameters obtained from the experiment in the previous chapter and comparisons prior to and after this operation were carried out using ultra-depth microscopy, as

illustrated in Fig. 6.1. The Fig. 6.1 (a) – (c), in the left column, were the morphology of contaminants under magnifications of 100, 1,000 and 2,000 times respectively. It can be observed in Fig. 6.1 (a) that the contaminants were in rough appearance, demonstrating the existence of particle depositions. The gloss (bright lines) on contaminant layers could be the reflection of light from the microscopy by liquid compositions and this was verified by Fig. 6.1 (b) and (c), which were taken under magnification of 1,000 and 2,000 times. Fig. 6.1 (b) and (c) demonstrated that the contaminants had a smoother surface, under a greater magnification, in comparison with Fig. 6.1 (a), because the oil covered the surface of particle depositions. Results after SC-CO_2 cleaning are illustrated in Fig. 6.1 (d) – (f). There were still apparent residual contaminants on the substrates, which were the non-extractable compositions e.g. carbon depositions and inorganic dust particles. Cracks can be observed on the surface of residues from a 100 times magnified image in Fig. 6.1 (d). And the gloss at the edges of the particles had vanished with the elimination of liquid compositions by SC-CO_2, revealing the original colour of the particle depositions. The contaminant structure had also changed after treatment using SC-CO_2; for instance, micro cracks can be observed on the surface of contamination layers. Pores were formed in the contaminants, as illustrated in Fig. 6.1 (e), due to the elimination of liquid component that provided adhesive forces for particles to form stable and solid structures. In this action, the residues had been loosened by the cracks and holes were formed during SC-CO_2 cleaning. However, the shear forces by flowing fluid were not adequate to overcome the adhesive forces between the “dry” particles. Consequently, further operations are required to remove residual contaminations.

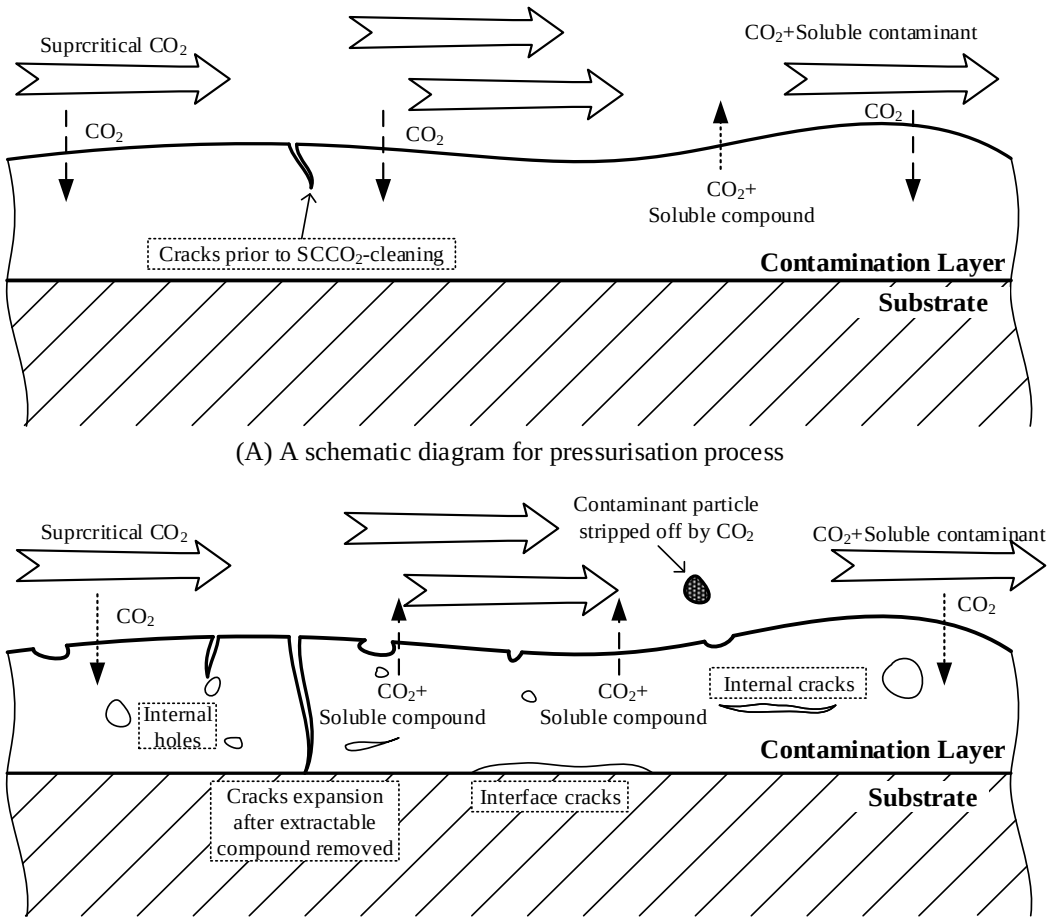

Fig. 6.2 The schematic diagram for the decontamination of SC-CO_2 cleaning

Based on the analysis of the morphology changes of contamination, a schematic model was proposed to describe the contamination removal on a decommissioned engine using SC-CO2. Contaminants were a mixture of organic liquid, carbon depositions and other compounds with very high molecular weight, adhering to the surface as depicted in Fig. 6.2 (A). When CO_2 was charged into the cleaning vessel, the fluids transformed into supercritical status gave rise to mass transfers between the supercritical fluid and contaminant layers. In the mass transfer, CO_2 molecules penetrated contaminant and dissolved in the liquid

compounds; simultaneously, soluble compounds also diffused into the flowing fluid and were taken away by CO_2 streams. In the initial stages, it was primarily the dissolving of CO_2 that dominated the process and removal mechanism was due to the erosional effect from the flowing supercritical fluid.

6.2 A Comparison between New and Conventional Methods

The cleaning study was carried out based on engine lubricating oil and grease and the optimum technological cleaning parameters were obtained by studying the effect of temperature, pressure, time, flow rates and co-solvents. Results showed that SC-CO_2 demonstrates potential for the removal of oily contamination. However, the removal of residual surface contamination using this method requires further investigations. This section therefore presents the results of a comparative cleaning study between SCF and thermal cleaning, using decommissioned engine components as the samples.

Thermal cleaning is one of the commercially used pre-treatment processes in the cleaning of engine cores. When hot stream or high temperature is added into the cleaning apparatus, oily contamination on the cores is evaporated or combusted, leaving the residue with a loose and porous structure that can be easily removed due to the dramatically reduced adhesive forces. Although contamination removing can be achieved in the engine's components, the limitations of thermal cleaning are obvious: (1) because of the use of high temperature, thermal cleaning is not applicable for flammable parts or those with low melting point; (2) the process is high in both energy and time requirements, to ensure the combustion and vaporisation of contaminants; (3) the heating and cooling can alter the cores'

surface properties, affecting the quality of remanufactured products; and (4) combustion of organic contamination generates CO_2 and airborne contaminants, contributing to global warming and clearly inconsistent with the ethos of sustainable manufacturing. An improved or alternative method of cleaning is therefore proposed for the remanufacturing by use of supercritical CO_2.

Samples were pre-treated independently, either with SC-CO_2 or by thermal cleaning; subsequently, abrasive water jet cleaning and ultrasonic cleaning were used separately to remove the contaminants. By comparing the different combinations of pre-treatment and cleaning, each method's performance is obtained and evaluated.

6.2.1 Apparatus and Materials

Supercritical fluid cleaning was performed in the same test rig. As it was equipped with a 1 L cleaning vessel, which was small, the components selected for the comparative experiment used rocker arms, valves, tappets and so on. The thermal cleaning process was conducted in a heat treatment furnace type SX12-10 manufactured by Hangzhou Deju Equipment, with internal dimensions 500×300×200 cm. The ultrasonic cleaner has a 10 L cleaning vessel and operates at 40 kHz. Cleaning can be achieved from 0 to 50 °C with durations up to 30 min.

Two typical kinds of contamination, commonly observed on the surface and inside engines, were selected as the cleaning objectives: oily contamination and engine carbon deposition. These were chosen due to the specific properties of CO_2: non-polarity, which, it was hoped, would allow the SC-CO_2 technology to remove engine oil and lubricating grease; and high diffusion force, allowing it to permeate

the heavy carbon deposition and thus loosening carbon deposition. Due to the volume of the cleaning vessel, small parts such as nozzles, cylinder bolts, rocker arms and rocker shafts were used for the oil cleaning process, whilst the experiments to remove carbon deposition were carried out on valves. The cleaning solvent was SC-CO_2 of 99 % purity.

6.2.2 Experimental Procedures

As depicted in Table 6.1, the experimentation was divided into two stages and was conducted in six different combinations. In the experiments numbered from to 4, each of the samples was treated by a pre-cleaning process of SC-CO_2 or thermal cleaning, respectively. The remaining contaminants were then removed either by abrasive water jet or ultrasonic cleaning. Another two groups of samples (tappets, valves and rocker arms) were cleaned without pre-treatment and are numbered 5 and 6 in Table 6.1.

Table 6.1 Cleaning procedure designing

Number	Pre-cleaning method	Post-cleaning method
1	Supercritical CO_2	Abrasive water jet cleaning
2	Supercritical CO_2	Ultrasonic cleaning
3	Thermal cleaning	Abrasive water jet cleaning
4	Thermal cleaning	Ultrasonic cleaning
5	No treatment	Abrasive water jet cleaning
6	No treatment	Ultrasonic cleaning

Samples cleaned by supercritical fluid were soaked in the CO_2 atmosphere for 40 min, at a pressure of 25 MPa and a temperature of 75 °C, with a CO_2 flow rate of 6.8 l/h using 5 % ethanol as a co-solvent.

Thermal cleaning was carried out at 427 °C in accordance with recommendations. The ultrasonic cleaner (40 kHz) was set to 50 °C, allowing most of the residuals to be removed within 15 min. Abrasive water jet cleaning was carried out for 5 min with 0.3 MPa injecting pressure and a grinding: liquid ratio of 3:18. Meanwhile, the samples that were not pre-treated went through the cleaning process for three times the duration of the pre-treated samples.

6.3 Results of Retired Engines Cleaning on SC-CO_2

A series of components from scrapped engines was used in the experiment, but only representative results are illustrated in the Figures in this section. For the full results of different cleaning methods and their combinations, please refer to Appendix C. Fig. 6.3 illustrates a tappet that had not been cleaned by any process. Black adsorbate of oil and other contamination on the surface of samples is viscous and is widely distributed, both on the surface and in the internal structure, which makes it removal difficult.

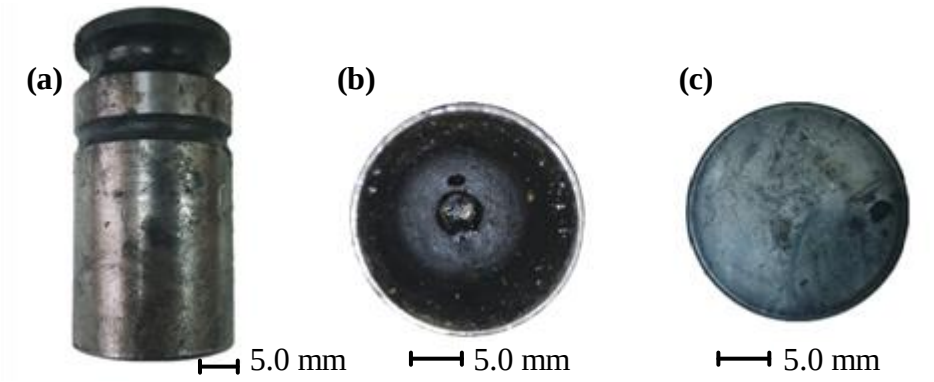

Fig. 6.3 A recovered tappet from retired engines, prior to being cleaned

(a) – Tappet, (b) – Tappet interior, (c) Tappet top

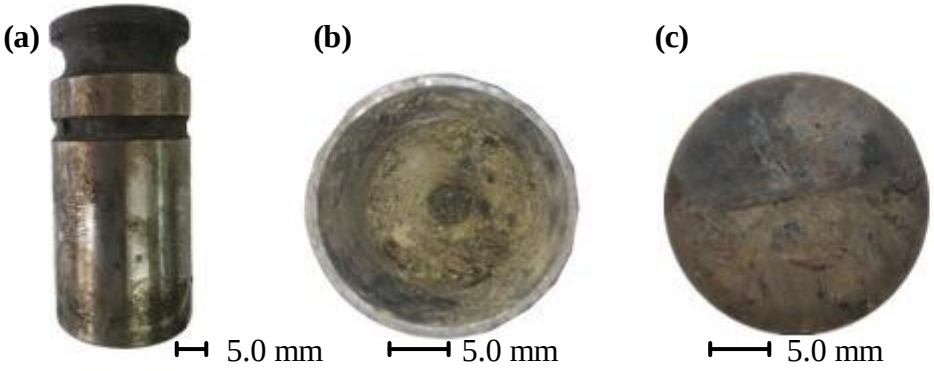

Fig. 6.4 The tappet after SC-CO_2 treatment

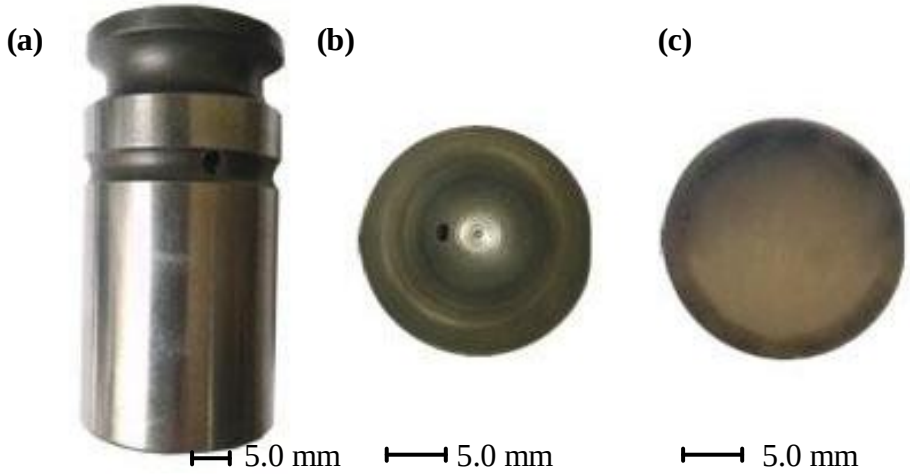

Fig. 6.5 The tappet after test No. 1: SC-CO_2 followed by abrasive water jet cleaning

After soaking in the 75 °C supercritical CO_2, the viscous contamination on the samples became very loose. However, the black colours visible in Fig. 6.4 demonstrate that carbon deposition cannot be removed by the SC-CO_2 cleaning method only. Following the pre-treatment, each sample was then cleaned by either abrasive water jet cleaning or by ultrasonic cleaning. Fig. 6.5 shows the samples after abrasive water jet cleaning: the combination of supercritical CO_2 pre-

treatment with abrasive water jet cleaning significantly improved the samples; it appears that this could solve the problem of removing carbon deposition on engine, which has been a big problem for the commercial cleaning of engines. In comparison, Fig. 6.6 demonstrates no obvious residue subsequent to ultrasonic cleaning, but with the downside that some oxidation remained, together with the incomplete removal of contamination from the corners.

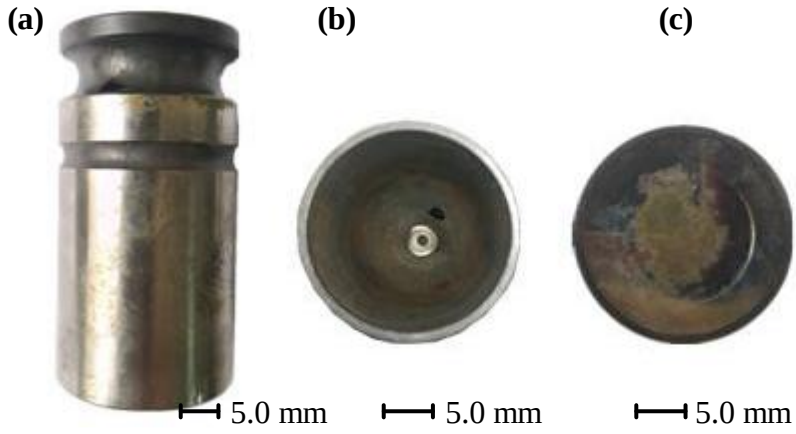

Fig. 6.6 Samples after test No. 2: SC-CO_2 followed by ultrasonic cleaning

Fig. 6.7 Samples cleaned by thermal cleaning

Thermal treatment, for tests 3 and 4, followed the protocol outlined in 6.2.2. As with the SC-CO_2 pre-treatment, the contamination appeared to be loosened, but turned to a rust-like colour (see Fig. 6.7), whilst the samples themselves turned dark. This implies that the surface carbon had been decomposed, and some oxidation reactions had occurred on the sample materials. After the cleaning as per experiments 3 and 4, the results can be seen in Fig. 6.8 and Fig. 6.9. Apparent removal of the contamination can be observed in the samples by this method, whilst the surface of samples all turned into dark grey. This is because of the oxidation of iron under the high temperature of thermal decomposition. Temperature of this process had big influence on oxide type of the product as shown in Figs. 11 and 12 shows similar results to those with SC-CO_2 pre-treatment, except that the black oxide layers due to the high temperature could not be removed (Fig. 6.10).

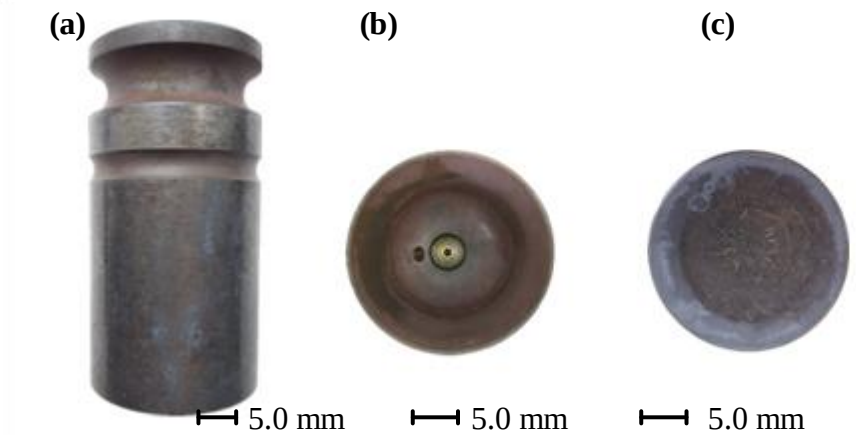

Fig. 6.8 Cleaned samples of test No. 3: thermal cleaning followed by abrasive water jet cleaning

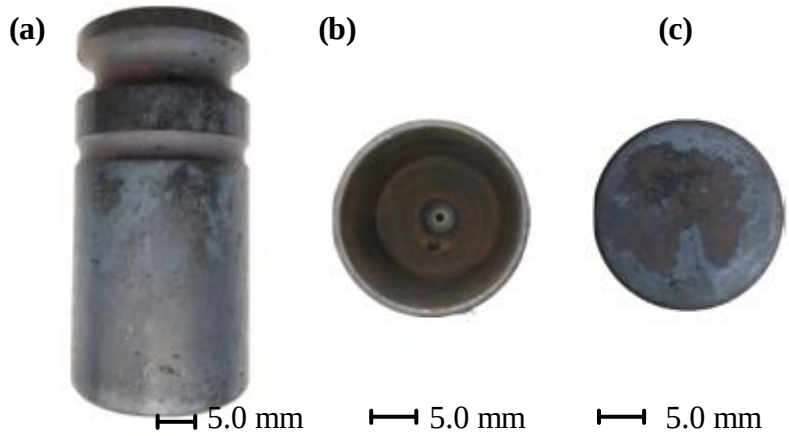

Fig. 6.9 Cleaned samples of test No. 4: thermal cleaning followed by ultrasonic cleaning

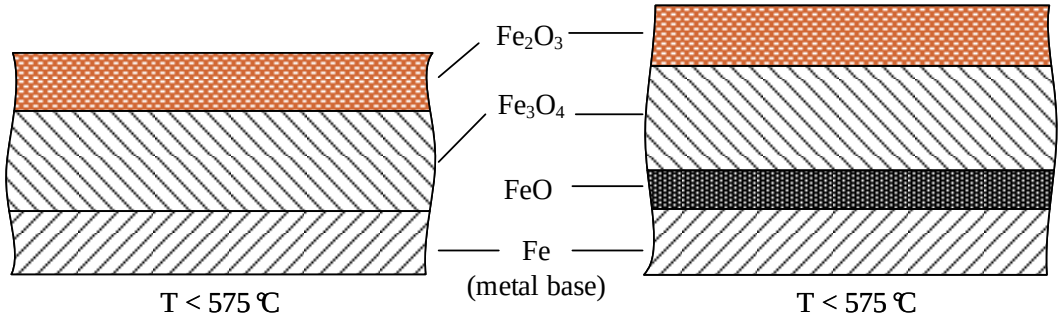

Fig. 6.10 The composition of iron oxide at different temperatures

The previous four tests illustrate outstanding cleaning effects, showing that the majority of contamination can be removed by any of the four combinations. To clarify the impact of the pre-treatment in contamination removal, tests numbered 5 and 6 were carried out, test 5 using only abrasive water jet cleaning and test 6 using only ultrasonic cleaning. As noted above, the duration of test 5 was three times that of tests 1 and 3. The results of abrasive water jet cleaning are shown in Fig. 6.11, including abrasive particles that have adhered to the oily contamination due to the latter's viscosity. Only around 20 % of the contamination was removed

from the tappet surface whilst hardly any was removed from the interior. The majority of the carbon deposition on the valve was removed but abrasive particles were absorbed in the residual viscous asphalting, which made it hard to be cleaned. Test 6, using only ultrasonic cleaning, again was carried out for three times the duration of tests 2 and 4. There was residue evident on the surface of samples, along with a large quantity of carbon deposition. In Fig. 6.12, obvious oxide spots can be observed on the surface of samples together with residue in the corners.

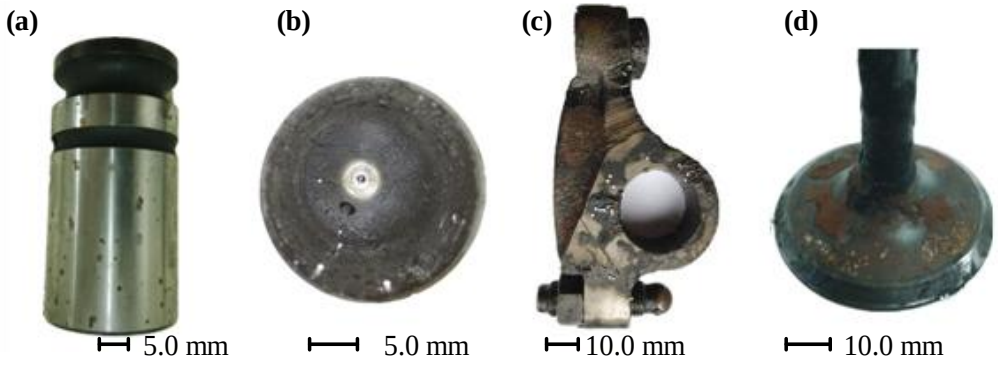

Fig. 6.11 Results of cleaning with abrasive water jet alone

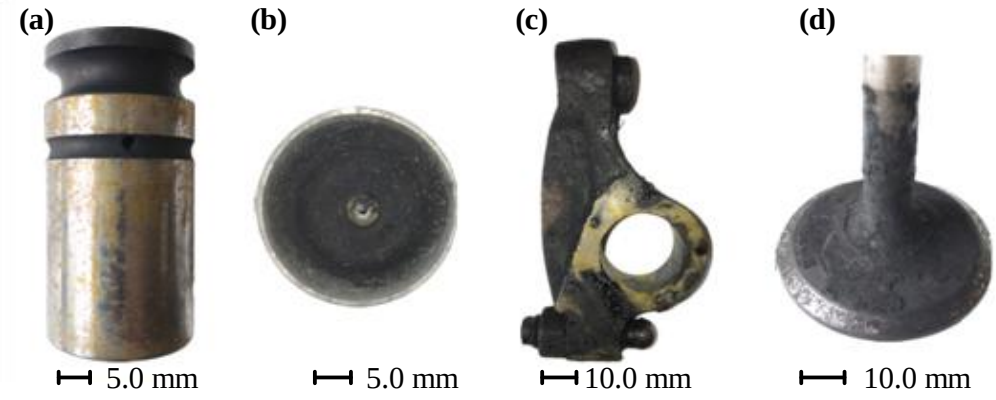

Fig. 6.12 Cleaning results with ultrasonic treatment alone

It was noted in the Test result section that the use of heat as a pre-treatment

may alter the material properties of the samples. For instance, tempering after the thermal process can decrease the hardness of the samples. Thus, hardness testing was carried out on the tappets, rocker arms and rocker shafts in tests 2 and 4 using a Rockwell Hardness Meter, both before and after cleaning. The results of these tests are shown in Table 2. It can be seen that samples cleaned by supercritical CO_2 exhibit minimal variation in hardness, whilst samples that have gone through the thermal cleaning process have drastically reduced hardness. Hardness changes in the thermal cleaning indicated that tempering happened during the cooling downtime, whilst the supercritical CO_2 pre-treatment was more moderate, causing minimal changes to material properties.

Table 6.2 Rockwell (HRC) hardness of test samples

Sample category	Test number	Original/HRC	Final/HRC
Tappets	2	56.2	56.2
	4	56.2	51
Rocker arms	2	60.3	60
	4	60.2	40.6
Rocker shafts	2	62.4	62
	4	63.1	57.9

6.4 SC-CO_2 Cleaning of Paint Layers

Paint layers are designed to be robust to survive adverse conditions (Chen et al., 2010). Accordingly, the removal of these coatings is more difficult to achieve than that of the other substances. Research of the coating removal using laser method (Chen et al., 2010, Daurelio et al., 1999), ultrasound (Reinhart, 1989), conventional aqueous cleaning methods (Wolbers, 2000), dry-ice cleaning (Spur et al., 1999) and blasting cleaning (Raykowski et al., 2001, Momber, 2007) has

been widely studied.

Each method has associated environmental impact. During laser cleaning, a focused laser beam combusts paint layers; the small dimension of laser restricts the efficiency of the cleaning process. Hazardous gases emitted during laser cleaning are also an inevitable environmental issue when batches of cores are cleaned. Using organic materials or other chemical removal technologies, aqueous cleaning is problematic from environmental considerations, as it involves various forms of more or less hazardous solvents and detergents (Sivakumar et al., 2009). As dry-ice cleaning sublimates into the atmosphere immediately after the cleaning process, its industrial application aggravates the greenhouse effect. There could be much dust pollution during the conventional blasting cleaning (Balan, 2008), which can be harmful to the operators. By adding the water into the shot blasting system, pollution can be significantly reduced.

In addition, for end-of-life products, there are usually other organic or inorganic mixtures of contaminant of on the surface or the paint layers, making the situation complicated. Previous chapters have demonstrated that the combination of supercritical carbon dioxide (SC-CO_2), as a pre-treatment process, and liquid blasting, as the removing means, has the feasibility of removal oily contaminant on a core surface. When these contaminants are on the paint layer, which is commonly observed, the cleaning situation could be different. Considering that the paint is of organic composition, the feasibility of SC-CO_2 treatment requires study.

The feasibility of the proposed cleaning method is studied on the paint layers. Coatings are studied without the existence of other type of contaminants; stainless

steel specimens are artificially coated with the metallic paints to mimic the real coatings on the remanufacturing cores. The experiment show results consistent with the theoretical analysis of the mechanism of SC-CO_2 treatment. Single-particle shot experiments and liquid blasting cleaning were conducted using the specimens from a previous treatment, illustrating that liquid blasting cleaning is more effective when accompanied by SC-CO_2 treatment. Although the efficiency of this process is not yet as high as other methods, this combination of the methods provides an approach to cleaning the paint layers which could prove more environmentally friendly.

6.4.1 Mechanism of SC-CO_2 Treatment in Paint Layers

SC-CO_2 has low viscosity and extremely low surface tension. Consequently, in the supercritical status, the CO_2 molecules diffuse effortlessly into the internal structure of the paint layers. In a certain residence time, the long-chain organic compounds in the layer become porous. This phenomenon has been widely used in the synthesis of porous materials by researchers (Cooper and Holmes, 1999, Cooper, 2003). The foaming theory, describing the behaviour when an organic substrate contacts an SCF, is one of the widely accepted theories and is the main mechanism utilised in the treatment process in this paper. Many models have been established to explain the foaming phenomenon, of which the bubble nucleation theory is widely used (Frayssinet et al., 1998, Goel and Beckman, 1995). In the supercritical condition, CO_2 molecules diffuse inside the polymeric substance becoming a homogeneous system. During the rapid decompression, CO_2 molecules in this system aggregate as a result of the nucleation, developing a tremendous amount of micro bubbles inside the polymer. These bubbles gradually

gather and grow bigger until the swelling force reach equilibrium with the resistance, eventually forming cellular structures in the polymer. The walls between two bubbles bear the tensile stress, which is generated during the expansion becoming bigger. However, the wall may eventually rupture as a result of the expansion of these bubbles; the bubbles, then join together to form a larger one, as illustrated in Fig. 6.13.

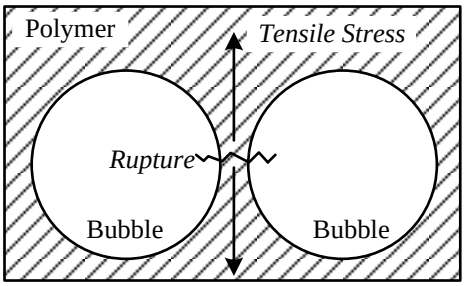

Fig. 6.13 The merger of bubbles and the rupture of the wall

Based on this theory, the treatment using the SC-CO_2 can be divided into three processes. Firstly, the CO_2 molecules, in a supercritical condition, diffuse into voids within the paint layer, becoming a homogeneous phase with the paint. During the rapid decompression process, CO_2 becomes supersaturated in this homogeneous phase and it is decompressed too rapidly for CO_2 molecules to escape from the layers; clusters of molecules aggregate into micro bubbles in the paint. Eventually, tensile stresses because of the pressure difference between the bubbles and the atmosphere ruptures the walls between adjacent bubbles, generating larger bubbles. Cracks form in different positions in the layers, as depicted in Fig. 6.14, i.e. interfacial cracks, internal cracks and surface cracks, as the results of bubbles generated in different positions. The generation of the bubbles increases the thickness of the layers and some will split the paint surface.

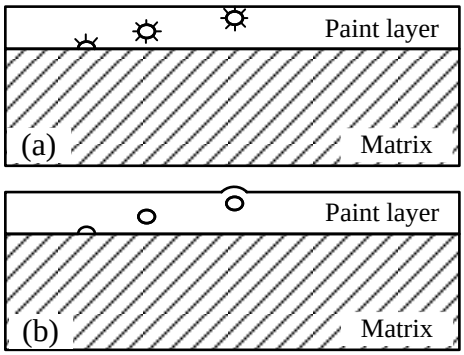

Fig. 6.14 Schematic diagram of crack formation in paint layers

The thermal effect is another notable factor employed in the SC-CO_2 treatment. The temperature in the supercritical condition is over 40 ℃; thermal expansion acts on both the paint and the matrix. However, the expansion coefficient of the two materials differs and the paint layer is in viscous flow state; consequently, the stress between the two materials is redistributed at this temperature. The linear coefficients of thermal expansion for the epoxy paint and stainless steel are 6.0×10^{-5} and 1.01×10^{-5} $℃^{-1}$ respectively. Once the system is quickly decompressed, tensile stress between paint layers and the matrix is formed as a result of the thermal contraction induced by the decreasing temperature. When the stress inside the interface is higher than the strength of the paint layers, there will be channel cracks and transverse cracks on the layer surface.

6.4.2 Experiment Materials and Procedures

Single-particle shot test and liquid blasting cleaning was carried out on a cleaning equipment. It was modified from the YT0-1308 grit blasting machine manufactured by the Beijing Dotel and FU22A air compressor manufactured by Fusheng. The reconstruction was carried out on the control cabinet, the spray gun

and the air supplying pipe. In Fig. 4.5 is the reconstructed control cabinet. Two switches were added, namely function selection button in black and the single particle button in green at the bottom, to achieve the wet blasting and single particle shooting functions in one equipment. Fig. 4.5 (b) illustrates the change inside the spray gun. Particles inside the hose are siphoned by the compressed air from the pipe next to the hose. The single-particle impact system was regulated at pressure between 0.2 MPa – 1.0 MPa. Fig. 4.5 (C) is the bottom view of the spray gun and the global view of the reconstructed facility is illustrated in Fig. 4.5 (d), with the specimen fixture that can adjust the spray angle. In this paper, the incident angles, in Fig. 6.15, were all fixed at 90 °to study the effect of single particle shot and liquid blasting on the paint removal.

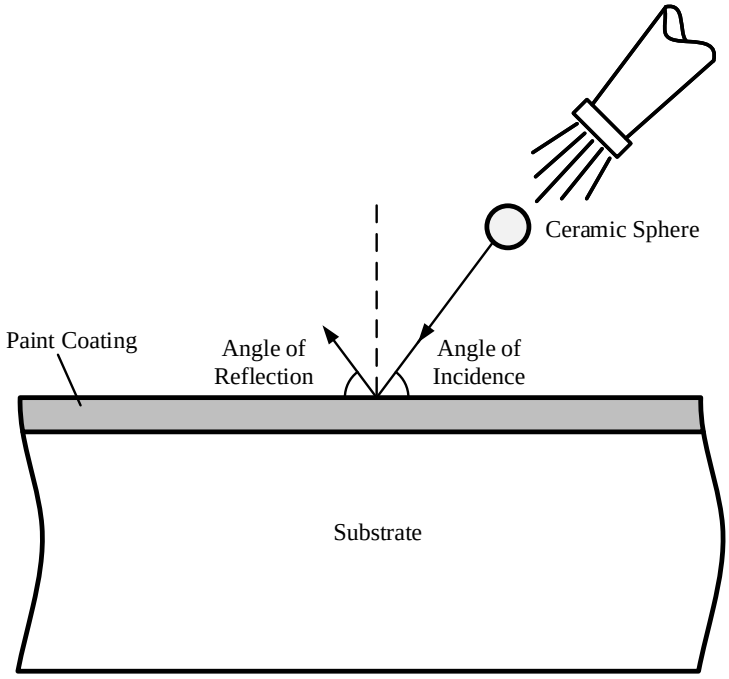

Fig. 6.15 A schematic diagram of the shot blasting cleaning by the reconstructed apparatus

In the remanufacturing industry, paint layers are mainly on the surface of cores. It is difficult to obtain identical paint layers with same thickness and performance using these real cores and the dimension of the experimental treatment vessel restricts real components in the process, as well. Consequently, the experiment was carried out using specimens instead to study the parameters involved in the cleaning process. Specimens were 304 stainless steel substrates of size 50×25×2 mm, coated with the epoxy micaceous iron oxide paints. The steels were polished by #400 and #600 sandpapers and measured using the roughness tester to guarantee the roughness deviation of different substrates less than 5%. Steel substrates were then soaked in acetone and cleaned by ultrasound. Spray was applied in a spray booth. The thickness of one spray was 0.02 mm and the final thickness was controlled by the spraying times. After each spray, specimens were left to stand for 20 min before the next application until the expected thickness was achieved; the samples were then naturally dried for 2 months. All the processes above guaranteed the robustness of the paint layers to mimic the actual coatings on the cores. CO_2 for the supercritical treatment was of 99 % purity.

Table 6.3 Composition of the ceramic grit

Ingredient	ZrO	SiO	Others
Mass Fraction	68%	31%	1%

Table 6.4 Physical properties of the ceramic grit

Specific Gravity	Bulk Density	Mohs Hardness	Granularity
3.85	2.36 kg/l	7.7	90%

Ceramic grit was used as the abrasive media in the liquid blasting cleaning process. Its chemical composition and some of the physical properties is shown in

Table 6.3 and Table 6.4. The ceramic material in blasting does not contaminate the component surfaces and the performance after blasting is more stable. Also the density of a ceramic material is relatively low, which consequently lowers the energy consumption of propulsion during the blasting process. It is widely found in industrial use for mould cleaning and oxide scale removal (Litchfield et al., 2006, Tolpygo et al., 2001). Grit was selected individually before the blasting process to ensure that each particle had similar granularity and dimension; the final grit was shown in Fig. 6.16.

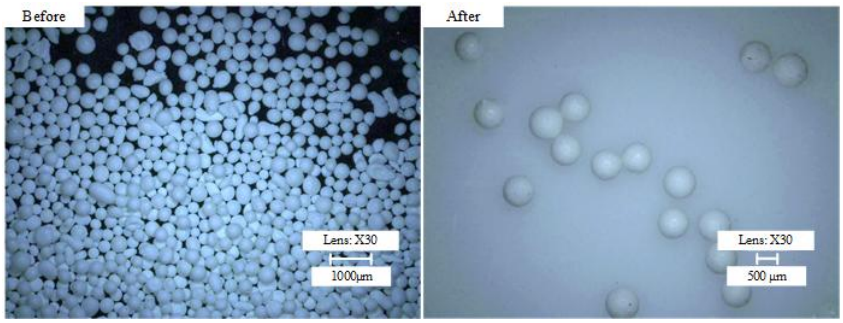

Fig. 6.16 Ceramic grit before and after the selection

The treatment using SC-CO_2 was implemented in the vessel of the apparatus, TC-SFE-50-1-120S laboratory apparatus. As depicted in Fig. 6.17, the pressure was raised to a given value and went through the dwell process; after this process, CO_2 was quickly released to the pressure of atmosphere. Morphology of these specimens was inspected by microscopy and ultra-depth microscopy. Table 6.5 indicates the range parameter employed to investigate the effects, i.e. dwell duration, pressure, temperature and the paint thickness, in the SC-CO_2 treatment process. These specimens treated by SC-CO_2 were then treated with a single-particle blasting experiment and liquid blasting cleaning to obtain the suitable

cleaning parameters in the painting layer removal.

Table 6.5 Experiment parameters of SC-CO_2 treatment

Group	Dwell duration/h	Pressure/MPa	Temperature/℃	Thickness/mm
Pilot	0.5	25	40	0.1
1	0/1/2	25	40	0.1
2	0	10/15/25	40	0.1
3	0	15	40/60	0.1
4	0	25	40	0.06/0.1/0.2

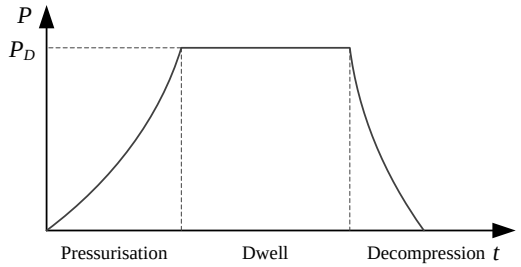

Fig. 6.17 Pressure curve of SC-CO_2 treatment against time

6.5 Results of Paint Layers Removal Using SC-CO_2

The appearance changes of paint layers were analysed subsequent to the SC-CO_2 treatment, then the residual paints were removed by liquid blasting. The cleaning results are discussed in this section.

6.5.1 Appearance Changes

The pilot experiment was designed primarily to study how the SC-CO_2 affects the morphology of the paint layer. Specimens in this group were coated with 0.1 mm thick paint and placed in a treatment vessel in which SC-CO_2 was pressurised to 25 MPa and heated to 40 °C for 0.5 h. The vessel was quickly decompressed to

the atmospheric pressure and specimens were the taken out for inspection. The treated specimens were compared with the originally smooth appearance. As illustrated in Fig. 6.18, there was no distinct change immediately after the specimen was taken out. However, after being exposed to the atmosphere for 1 min, white substances emerged on the layer surface though the layer itself had no distinct changes. The white substance was the vapour de-sublimation because of specimens rapid cooling down by the decompression. After 2 min, the paint layer began to swell and was covered by more white substances, which was proved to be ice crystals. These crystals vanished in 3 min after the exposure and a bubble-like appearance was observed accompanied with cracking sounds. The cracking sounds were due to the fracture of paint layers because of inflation and tension stress inside the layer.

The other four groups of experiment were designed to study the effects of different parameters on treatment, namely dwell duration, pressure, temperature and the layer thickness. Representative outcomes of specimens under different conditions are illustrated in Fig. 6.19. Apparent channel cracks and transverse cracks emerged and swelling developed in the centre of the pieces fragmented by these cracks when the vessel was immediately decompressed without dwelling. However, when the dwell duration was 1 h or 2 h, there were no apparent cracks and the thickness of the swelled pieces increased with the surface becoming uneven. This was also similarly observed in Fig. 6.18 (3 min), in which the specimen was soaked in the pressurised vessel for 0.5 h.

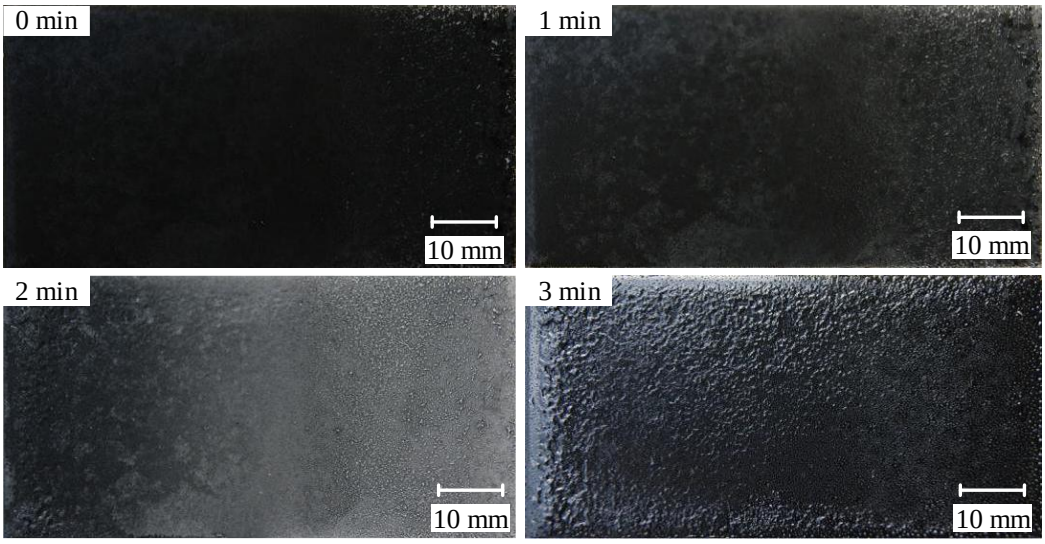

Fig. 6.18 Specimen appearance change against time when exposed to the atmosphere

When there is no dwell duration employed in the treatment, very few CO_2 molecules diffuse into the paint layers. The small amount of CO_2 molecules cannot resist the tensile and shear strength from the thermal contraction induced by the declined temperature after the decompression; consequently, the paint layer ruptures and cracks. When the dwell duration is increased to 1 h, there can been enough time for CO_2 molecules to form stable structures inside the paint layer. The cellular structure has sufficient elasticity to overcome the thermal contraction; this mechanism is also responsible for the observed results of dwell duration 2 h.

At pressure of 25 MPa, apparent channel and transverse cracks formed on the surface of paint layers (Fig. 6.19 – I). These cracks separated the paint layer into small fragments. At 15 MPa, the cracks were not sufficient to form the fragments like those at 25 MPa. However, it was not able to generate any cracks when at 10 MPa (Fig. 6.19 – II). This is because that there was insufficient pressure for CO_2

penetrating into the paint layer; consequently, when the system was decompressed, the high tensile and shear strength inside the paint layer induced more significant cracks and swelling.

After the treatment at temperatures of both 40 ℃ and 60 ℃, cracks could be observed on the surface of the specimens, according to the result depicted in Fig. 6.19 – III. At the higher temperature, paint layers swelled more significantly due to thermal expansion, leading to a greater volume. Assuming that the specimens were cooled down to 20 ℃ from 40 and 60 ℃, the displacements of paint were calculated to be 0.10 mm/m and 0.20 mm/m, respectively, as thermal contractions. The tensile and shear force inside the layers was greater as the result of a higher temperature difference. Therefore, the cracks were much wider at the higher temperature, but the fragments swelled less seriously.

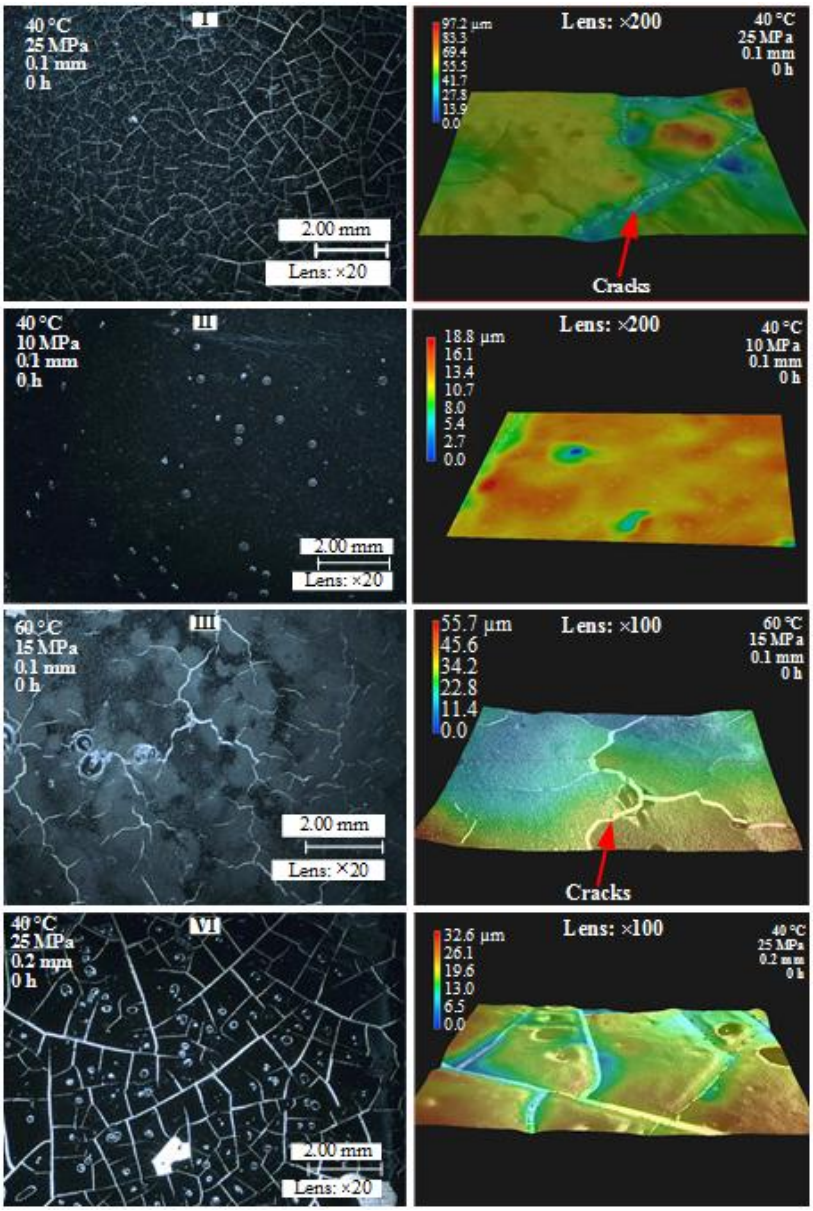

Fig. 6.19 Representative images and morphologies of paint layers under different conditions

I: 40 °C, 25 MPa, 0.1 mm, 0 h; II: 40 °C, 10 MPa, 0.1 mm, 0 h; III: 60 °C, 15 MPa, 0.1 mm, 0 h; IV: 40 °C, 25 MPa, 0.2 mm, 0 h;

The paint thickness is not a decisive factor for the generation of cracks during

the supercritical treatment, concluded from the tests with different thickness. At suitable temperature and pressure, the dimension of the cracks and the size of the paint fragments increased with the paint layer thickness (Fig. 6.19 – IV). However, the thick paint did not swell significantly as the thinner ones, because the thick paint layer had the capacity to absorb more CO_2 molecules and to distribute the molecules more uniformly.

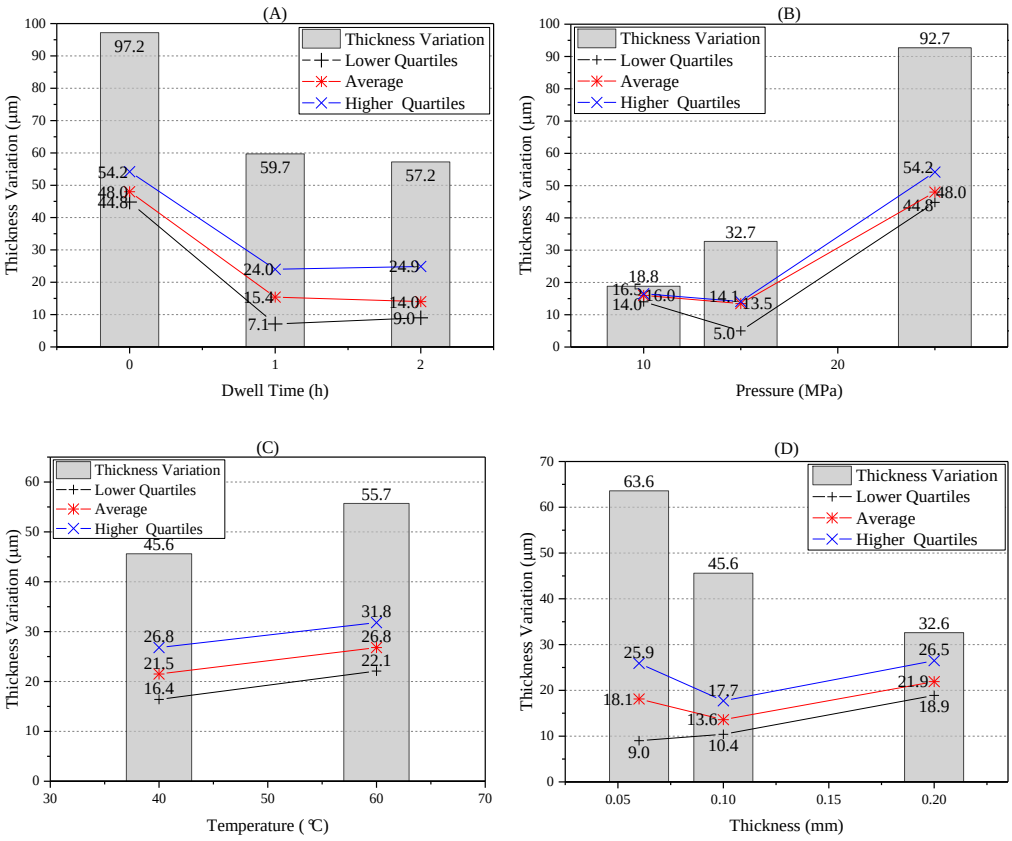

Fig. 6.20 Thickness Fluctuation of paints through different parameters

(A) Dwell duration, (B) Pressure, (C) Temperature, (D) Layer thickness

Fig. 6.20 illustrates paint height, average thickness and height of the lower and higher quartiles of the pixels in each image taken by ultra-depth microscopy;

the image data were analysed and collected by image processing software. In these figures, when the average height was much lower than the half of the total height, the swelled paint represents very sharp morphology, as illustrated in Fig. 6.19 – (I). On the contrary, the paint that swelled shows as relatively blunt morphology. Similarly, when the higher quartile is closed to the top the total height variation, the paint demonstrates sharper swelling; when the lower quartile is closed to the bottom, i.e. zero μm, it can be considered that great proportion of the paint did not swell and still adhered to the substrate material. By contrast, when the quartiles are close to the average height, it means that a large area of the paint has swelled, leading to easier removal from the substrates. In Fig. 5.20 (A), the specimens with one or two hours dwell duration shows the similar height distribution, indicating that the cellular structures inside had thoroughly formed. However, it has a negative effect on the generation of cracks, consequently impeding the removal of paint, which will be demonstrated in the following section. The height of paint increased with the pressure (Fig. 5.20 B) and temperature (Fig. 5.20 C), while declines with the increasing thickness. In the experiment range, the pressure and temperature had the positive effect in the generation of cracks while dwell duration was a negative factor and the thickness was not the decisive reason when the other parameters were suitable for the SC-CO_2 treatment.

6.5.2 Single-Particle Shot

Specimens in this test were grouped in Table 6.6. As it has been demonstrated that cracks were generated on the paint after an SC-CO_2 treatment. In this section, the experiments were designed to test the effect of propelling pressure and particle dimension on the removal productivity. Tests were carried out at the pressure of

0.2 MPa and 0.4 MPa, and 0.3 mm and 0.9 mm ceramic particles separately, using the specimens from the previous treatment process.

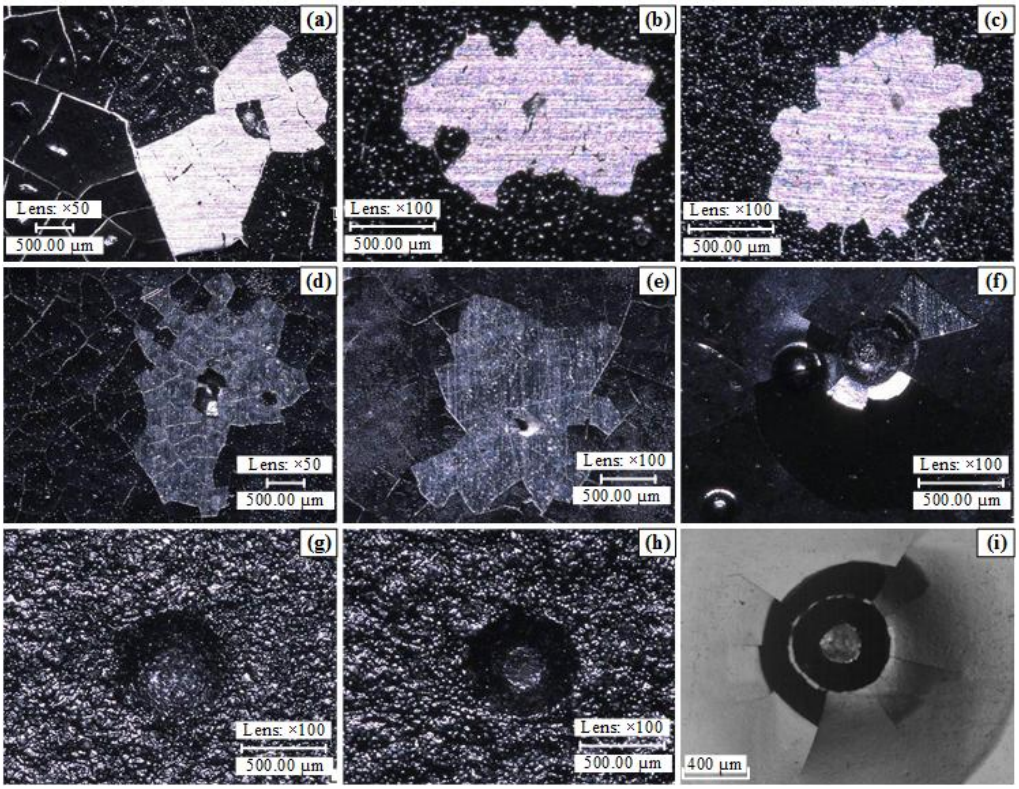

Fig. 6.21 Surface morphology of the specimen after single-particle shot under different treatment conditions according to Table 6.6

The removed areas were analysed by the image processing software (Image J V1.48, National Institutes of Health, USA). As the appearance in each group are similar under test parameters, the results taken by microscopy are selectively shown in Fig. 6.21. Evident removal had been achieved on the surface of those specimens with cracks in Fig. 6.21 (a) – (e). The removed sizes in these groups are compared in Fig. 6.22, which illustrates the result of group from Fig. 6.22 (a) to (e). The area of removed layers increases when the propelling pressure or the grit

diameter was higher. However, in the circumstance of using higher propelling pressure (0.4 MPa), there was damage on the matrix as a result of the high impact velocity. The test of using 0.4 MPa pressure and 0.9 mm grit was omitted as the damage on the matrix was an inevitable factor that should be taken into consideration when choosing the suitable cleaning condition. The best removal effect was achieved when using the higher propelling pressure and larger blasting particles.

Comparing the results of a, b and c in Fig. 6.21, it can be concluded that removal productivity increased on the thicker paint. Specimens in group f in Table 6.6, whose treatment pressure was low, retained the similar morphology with the specimen in Fig. 6.21 – (i) not being treated in SC-CO_2. The impact-induced coating morphology in these two groups were due to the indentation and the buckling delamination (Evans and Hutchinson, 1984) during the shot process. In the condition that the treatment pressure and temperature were higher, more paint fragments were removed by single-particle shot. The removal effect in group d was apparently better than that in group g and h, which means that it was easier to remove the paint layer if no dwell duration was employed in the treatment process. Fig. 6.21 (g) and (h) shows the cellular structures of the specimens with dwelling treatment. The cellular reduced the impact from the blasting shot particles; in the meanwhile, the stress from the shooting grit was effectively distracted. Consequently, no crack or removal was found on the surface of specimens in this group.

Table 6.6 Treatment condition of specimens in each group

Group	Pressure (MPa)	Temperature (°C)	Dwell duration (h)	Thickness (mm)
a	15	40	0	0.2
b	15	40	0	0.1
c	15	40	0	0.06
d	25	40	0	0.1
e	15	60	0	0.1
f	10	40	0	0.1
g	25	40	1	0.1
h	25	40	2	0.1

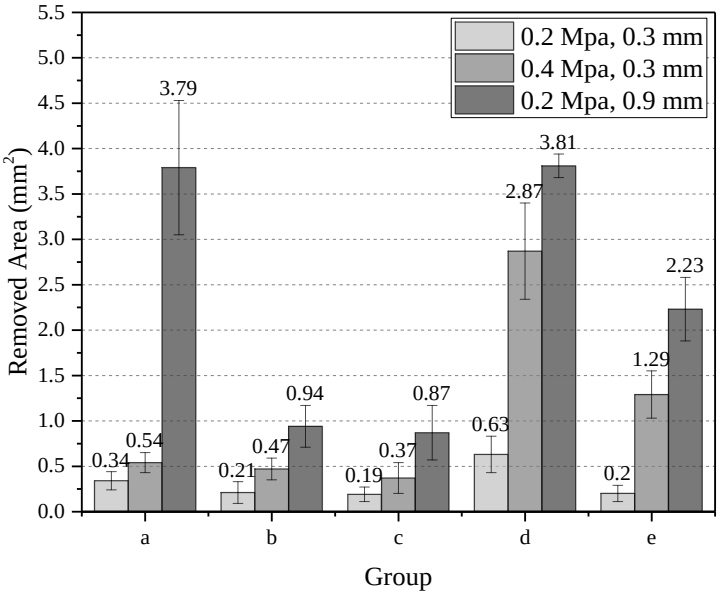

Fig. 6.22 Removed area by single-particle shot test under different impact conditions

6.5.3 Liquid Blasting Cleaning

Based on the single-particle study, experiment used the grit with the diameter of 0.75 mm propelled by the pressure of 0.3 MPa for liquid blasting cleaning. The 0.6 mm nozzle of the blasting apparatus moved in the velocity of 7×10^{-3} m/s,

spraying the liquid from 50 mm away to the specimens. Specimens with or without the SC-CO_2 treatment were blasted from one end to the other, with a solid/liquid volume ratio of 1:16.

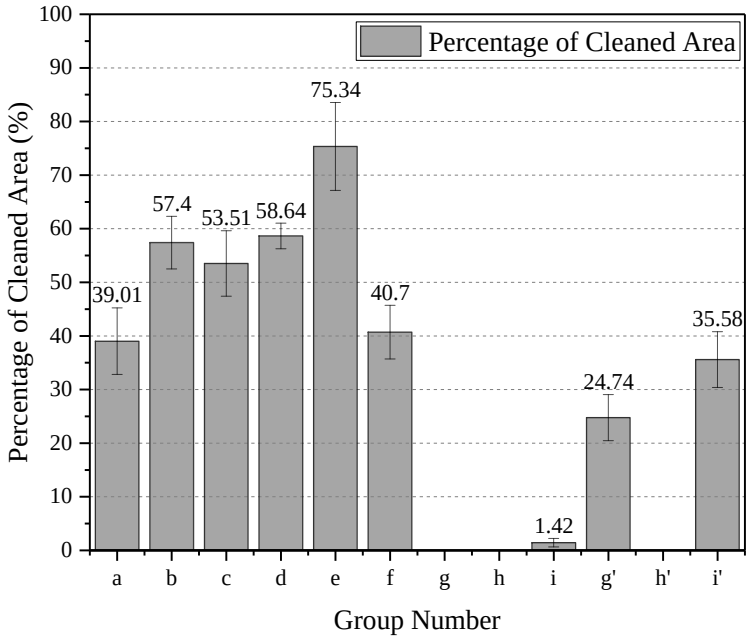

Fig. 6.23 The percentage of cleaned areas in each specimen

As illustrated in Fig. 6.24, the single cleaning process could remove most of paint on the specimens (a) – (e), while specimens of (g), (h) and (i) had not been cleaned effectively. The removal percentage, analysed by ImageJ, is depicted in Fig. 6.23. Although liquid blasting had removed some paints in Fig. 6.23 (g), (h) and (h'), there were obviously residuals on the cleaned area. Accordingly, the analysis of these three specimens was omitted and the cleaning operation in these groups are considered as failure. The amount of paint removed were similar independent of paint thickness. Better cleaning productivity was achieved when the treatment pressure and temperature were higher, e.g. specimen in Fig. 6.23 (e).

The cellular structure on those through the dwell process has reduced with roughly no removal effect. The result proved that there were bubbles inside the paint layers when specimens were soaked in SC-CO_2 for an excessively long time. The last three specimens were cleaned an additional two times, as shown in Fig. 6.24 (g'), (h') and (i'). The paint layer (i) without SC-CO_2 treatment was removed in large percentage, while the former two retained massive paint residues. Consequently, it has been deduced that dwelling time has a negative effect on effectiveness of liquid blasting.

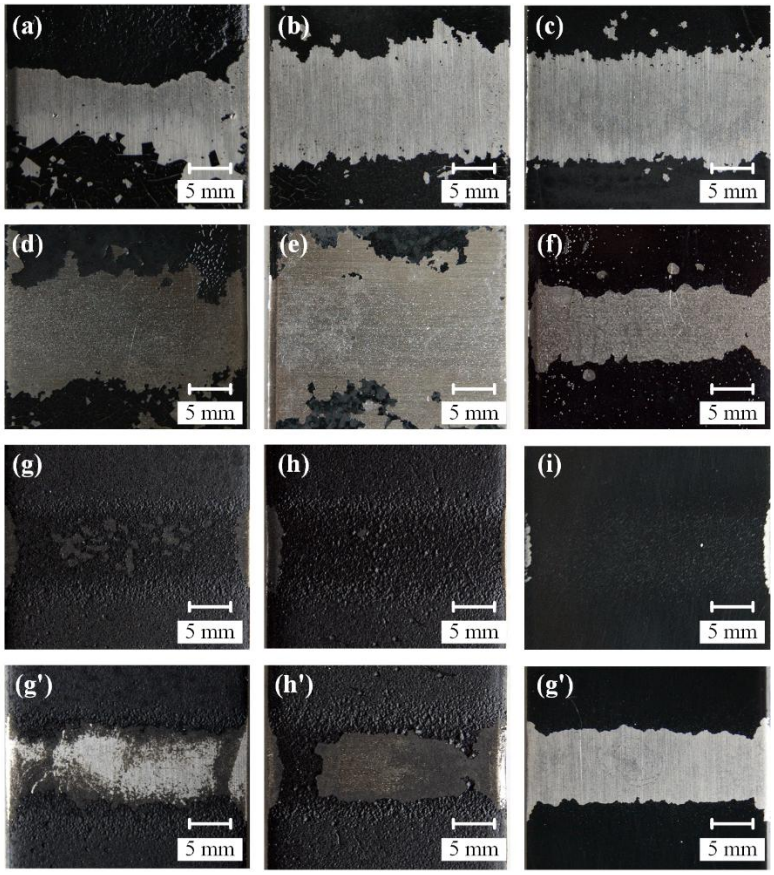

Fig. 6.24 Liquid blasting cleaning results of the specimens under different parameters in Table 6.6

6.6 Summary

The cleaning processes present an urgent problem to be solved in sustainable manufacturing, due to the environmental problems such as the use of chemical cleaning agents. Although commercially applied thermal cleaning methods can remove contamination, the negative effects such as degradation of surface properties, high levels of energy consumption and emission of greenhouse gases severely limit their use in a remanufacturing process that should only be positive for the environment. Its scope of application is also restricted to materials that are not sensitive to temperatures, such as irons and steels, while thermal decompositions are not feasible to clean substrates with low melting points, e.g. aluminium alloy.

This chapter conducted comparisons between SC-CO_2 and thermal pre-treatment as pre-treatment process, based on the cleaning of real components from discarded engines. Two different kinds of cleaning methods were also compared. It is noted that cleaning a small number of cores is both time and energy consuming and that the SC-CO_2 pre-treatment uses pressures that are relatively high compared to thermal cleaning. However, the visible cleaning results showed that (1) SC-CO_2 cleaning is an accessible approach for cleaning, and more materials can be cleaned by this method than by thermal cleaning; (2) Carbon emissions were rarely observed during the SC-CO_2 cleaning process because the CO_2 circulated within the apparatus; (3) SC-CO_2 has minimal impact on surface hardness, whilst thermal pre-treatment can drastically decrease the hardness.

The combination of SC-CO_2 cleaning as a pre-treatment followed by liquid

blasting cleaning demonstrates satisfactory cleaning results on the decommissioned engine parts. Based on this study, an extension of this combined "green" cleaning method was carried out on the removal of another commonly observed type of contaminants – paint coatings, whose removal is confronted by environmental issues, as well. The main mechanisms of SC-CO_2 treatment have been described using bubble nucleation theory and the thermal effect. Experiments have been carried out using specimens which mimic the real retired parts from the end-of-life products.

The combined cleaning experiment was carried out based on the cleaning of specimens mimicking the real paint layers on the remanufacturing cores. Different treatment parameters have been studied through the treatment process and single-particle shot experiments. After this, the liquid blasting has been used to clean the test specimens from the former process and specific cleaning parameters are selected based on the single-particle shot test. It can be concluded from the experiment that the temperature effects, bubble nucleation and swelling effects are the dominant mechanisms of treatment process using SC-CO_2. Dwelling time in the treatment process hinders the formation of channel cracks and transverse cracks; cracks can be only formed when the pressure reaches 15 MPa and the dimension of the cracks increases when the pressure is higher. Fragments segmented by the cracks are lager with increasing treatment temperature and with paint layer thickness. Even when the impacting velocity is relatively low, paint layers were removed by the blasting; increasing the impacting velocity or the diameter of the grit benefits the cleaning process, but higher velocities may also damage the surface of the stainless steel.

Thus, it can be concluded that SC-CO_2 cleaning is a promising alternative to thermal cleaning in commercial applications, especially when cleaning parts containing materials with a low melting point, such as aluminium. The combination of SC-CO_2 and liquid blasting cleaning promoted the productivity of the cleaning process; removal results were enhanced when treatment pressure or temperature was higher; specimens with thicker paint layers were cleaned most effectively. The possibilities of SC-CO_2 cleaning in large scales are well worth investigating for future study.

Chapter 7

Life Cycle Assessment

The previous chapter proposed a new cleaning approach using the combination of supercritical CO_2 as the pre-treatment and successive liquid blasting operations to remove residues. Experiments showed satisfactory cleaning results in comparison with the conventionally used cleaning method in the remanufacturing industry. The employment of carbon dioxide intuitively endowed this new combination environmentally friendly properties because CO_2 in this method was kept in a closed loop. However, whether the novel cleaning technology is environmentally preferable requires more scientific evaluation tools. This chapter used a standardised life cycle assessment (LCA) method to assess and compare the environmental performances of the newly proposed to the conventional cleaning methods.

7.1 Technological Background

One cleaning technology is usually not used alone in the remanufacturing industry but combined with other ones when confronting with the complex, serious and widely distributed contamination, which means that different cleaning methods would be used in one cleaning operation in succession to attain the required cleanliness. The employment of different cleaning technologies would

affect not only the eventual cleaning result but also the economic and environmental performance. Conventional cleaning operations in cleaning decommissioned engine parts comprised thermal decompositions as the pre-treatment and shot blasting as the succession to remove residues. A relatively novel combination of cleaning technologies was proposed in Chapter 6 used supercritical CO_2 and liquid blasting as the pre- and post-treatment, respectively.

The high-temperature cleaning system usually comprises a pre-treatment operation, known as the thermal decomposition (THD), along with a shot blasting to remove stubborn residues from the THD. This cleaning technology is exploited for the cleaning of organic contaminated metallic components such as oily/greasy contaminants on engines. It generally includes two steps. The contaminated component is firstly placed and heated in the combustion room of the THD facility, where the oily compounds in contaminants would be vaporised or decomposed by the large amount of heat, radiated on to the surface, from diesel or gas combustions. There could be solid residues adhering to the surface of the components after THD operation. The elimination of these residues is afterwards carried out by the blasting facility, which can recover the cleanliness to a required level. From the talk with workers in the Jinan Fuqiang Power Co., LTD, currently, all the solid wastes generated at the blasting stage are disposed through landfill. The thermal cleaning system is with properties such as high cleaning efficiency and automation by use of industrial smart meters, feedback adjustment elements, Programmable Logic Controller (PLC) system, etc..

The SC-CO_2 cleaning technology is a combination of SCF pre-treatment and liquid blasting by a shot blasting facility. In the SCF facility, oils and other

extractable compounds can be removed from the contaminant and the pollutant layers transformed into fluffy structures by the expansion effect result from temperature changes and bubble generation. The subsequent cleaning operation by use of liquid blasting (LQB) technology can remove stubborn stains, corrosion and residual contaminants with very little dust pollution to the atmosphere.

From the comparison between the two sets of cleaning systems, it can be concluded that the function of THD and SC-CO_2 are similar as pre-treatment operations, both using specific approaches to the removal of removable compounds from the contaminants. Both post-treatment methods use abrasive materials to clean the residues remaining on the component surfaces. As for the shot blasting, ceramic or steel balls used as the blasting medium exert impact on substrates, which causes heavy noises and dust pollution. Therefore, shot blasting cleaning is suitable for products with high hardness. By contrast, LQB cleaning was a smaller force on the products and could avoid local overheating on the substrates due to the cooling effect of liquid materials in the abrasives.

Considering the volume restriction of the laboratory SC-CO_2 cleaning test rig, study uses valves and cylinders that are typical parts in remanufacturing industry as objects. Specific technical differences are summarised in Table 7.1.

Table 7.1 Technical specifications of cleaning methods

Technologies	**THD**	**SC-CO_2 Cleaning**	**Shot Blasting**	**LQB**
Temperatures	315-530 °C	65-85 °C	/	/
Work durations	12-16 h per batch	Less than 2 h per batch	/	/
Feasible contaminants	Organic and other thermolabile substances	Oily, greasy or other organic substances	Rust, paints etc. with low viscosity	Rust, paints etc.
Feasible substrate materials	Materials with thermal stabilities	Precision components and thermal sensitive materials	Materials with high hardness and simple structures	Complicated-structure materials
Cleaning agents	High temperature gases	Supercritical CO_2	Metal or ceramic balls	Water and abrasive materials
Removing mechanisms	Changing the structure of contaminant by decomposed thermal sensitive substances	Dissolving soluble compounds and generating pores and cracks	By frictional forces from collision between abrasive and substrates	By scouring effect of liquids and abrasives
Advantages	Excellent performances for heavy oil contaminants; achievable for	Few pollutions; low operating temperature; preserving the original properties of materials;	Low cost; widely applicable;	Low cost; no dust
Disadvantages	Resulting in damages on the surface properties; not suitable for thermal sensitive materials and low melting point metals	High cost of SCF facilities; difficult with polymers due to the foaming phenomenon;	Not applicable for precise structures; dust pollutions	Noise pollution; sealed operation spaces

7.2 Methodology

LCA methodology is a scientific tool that can compare and evaluate the environmental performances of the two cleaning combinations. LCA is an internationally accepted technique to assess the environmental impacts of one product using structured, comprehensive and standardised management tools (ILCD handbook) and achieve objectives such as Material Flow Analysis, Environmental Risk Assessment, Ecological Benefit Analysis etc. (Finnveden et al., 2009). All stages of a product are taken into consideration in LCA, from raw material extraction through transportation, manufacturing, use, repair, disposal and decommission, i.e. from “cradle to grave”. A quantified result of different perspectives of the environment is outlined from a standardised LCA, which comprises four phases as follows (ISO, 2006):

1. Goal and scope: elucidate the reason for the study by demonstrating an explicit statement, which includes the context of the study, the readers to be communicated to and the definition of function unit and system boundaries.

2. Life Cycle Inventory (LCI) analysis: creates an inventory covering the material and energy flows from the input to output emissions within the life cycle of the study object related to the function unit.

3. Life Cycle Impact Assessment (LCIA): evaluates the significance of possible environmental impacts associated with human, environmental science and so on based on the LCI analysis from the previous phase.

4. Interpretation: is a systematic technique to summarise the results from LCI and LCIA, analyse results, provide conclusions and recommendations for further optimisation possibilities.

7.3 Goal and Scope Definition

In an LCA, the first step is to explicitly state the goal and scope of the study. This elucidates the context of the study and the readers to whom the LCA communicates.

7.3.1 Goal Definition

This study aims at carrying out comparisons on the environmental loads between the two cleaning technologies used in this thesis, for the removal of contaminants from decommissioned engine components and recognising the significant factors through quantitative assessment on material flows and energy consumptions. Spotlights were focused on impacts of different electricity resources for SC-CO_2 cleaning and the use of natural gas in different proportion in THD. In the meantime, the emission of exhaust gases (primarily carbon dioxide) from the two technologies were also discussed. Eventually, the comparative analysis will provide references for the parameter optimisation of SC-CO_2 operations from an environmental perspective.

7.3.2 Scope Definition

Fig. 7.1 shows the comparative flow diagram of the two cleaning technologies with the corresponding system boundary which demonstrates energy and material

flows through across the boundary. The “cradle-to-gate” method is used to demarcate system boundary because technologies do not involve the disposal phase, which is conventionally at the final stage of life cycle for one product. The partial life cycle in the system boundary includes raw materials, transportation, the cleaning process and treatment of wastes from cleaning operations.

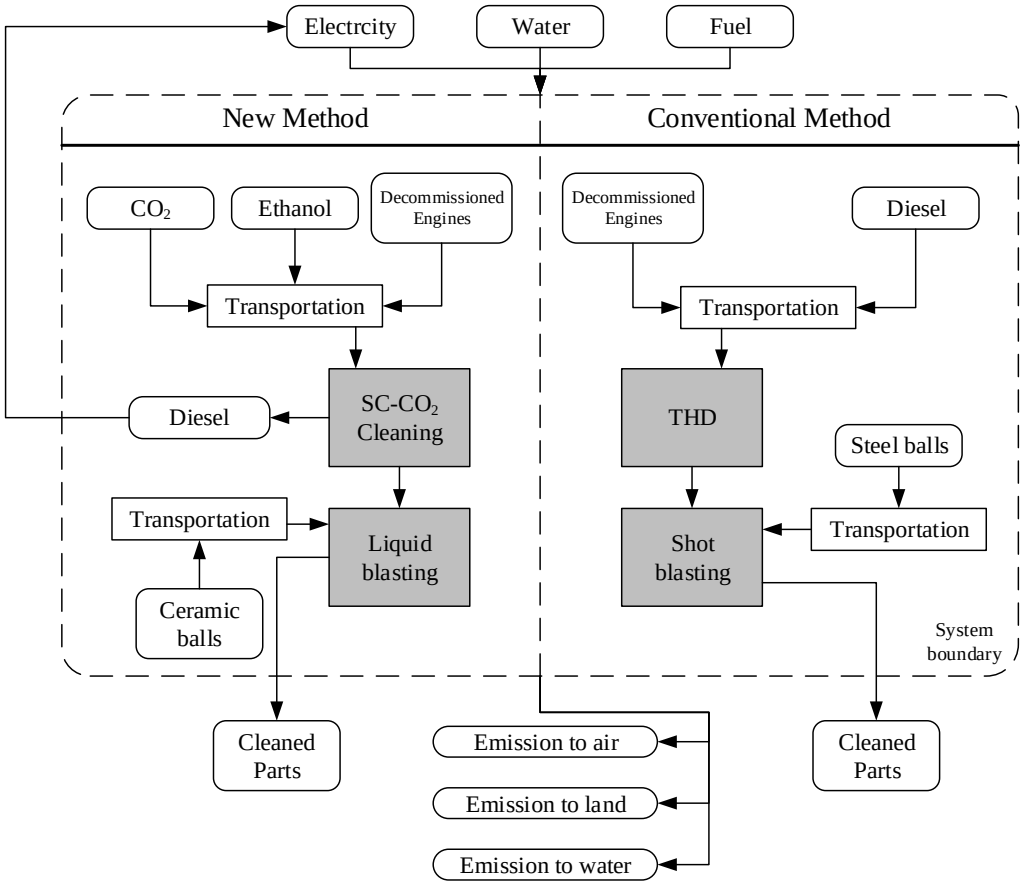

Fig. 7.1 Comparative flow diagram of two cleaning technologies and corresponding system boundary for scope definition

7.3.3 Function Unit

The two cleaning technologies are exploited for the removal of contaminants

on decommissioned engine parts, for instance paint layers or oil and carbon depositions. To remove contaminants completely from substrates is the ultimate goal in one cleaning operation. Therefore, the function unit for this comparative LCA is defined as “specific cleanliness achieved in removing oil and carbon depositions from one square metre of substrate”. Cleaning operations were implemented on WD 615 diesel engine cylinders.

7.3.4 Data Collection

For the new cleaning technology, the major input in SC-CO_2 and liquid blasting are electricity, along with a very small proportion of other materials such as ethanol, ceramic balls, etc.. As a new application area for SC-CO_2, this technology has not been widely accepted and used in industrial production. Therefore, the data for the new technology are primarily collected from the test rig, such as consumption of electricity, carbon dioxide, water and ceramic balls. A scale-up assumption for SC-CO_2 cleaning as an industrialised method is achieved by multiplying the laboratory data with a fixed coefficient (58), which was the ratio of average rated power of industrialised facility to that of the laboratory facility. Water in the SC-CO_2 test rig is used in the cooling and insulation systems to provide a stable operation environment. Ethanol is used as the co-solvent working in the cleaning vessel. Industrial data for these two substances are scaled up by multiplying a coefficient of the rated power of the apparatus used (industrial to laboratorial).

In a life cycle assessment, all energy consumption must be taken into considerations. Prior to the cleaning operations starts up, a ten-minute preheating

is required based on the formal operation process at a rated power of 486 kW. It is only required at the start-up phase for SC-CO_2 cleaning, after which the system starts to clean diesel cylinders at rated power of 580 kW. Twelve batches of cleaning can be achieved one day in the cleaning vessel, where the residence time is up to 30 minutes for each batch. Therefore, the energy consumption for one batch in the SC-CO_2 cleaning is calculated based on the equation as: $486\times10/(60\times12)\,\mathrm{kW\cdot h}+580\times\frac{30}{60}\,\mathrm{kW\cdot h}=296.75\,\mathrm{kW\cdot h}$.

Remaining data related with the two cleaning technologies has been summarised in Table 7.2. Data for SC-CO_2 cleaning process has been reasonably scaled up based on laboratory records collected from the experiment platform. Data for the liquid blasting process were collected from the laboratory and scaled up, similarly with the supercritical cleaning operation. Water, was a prominent substance in liquid blasting. Although it is recycled in the facility, inevitable loss could happen during normal operations and replacing old abrasives after several days of cleaning. With respect to the SC-CO_2 cleaning facility, the amount of water could be omitted because it was maintained in a closed loop without leaking and water would not be released once the facility started to work. Therefore, the total water consumption was considered only as in the liquid blasting operation and assigned to each cylinder. For the conventional cleaning technology, data were obtained through investigations and communications with the workers in SINOTRUK™, Jinan Fuqiang power Co., LTD. One batch cleaning of cylinders by the conventional method contained 26.8 function units. The new technology was accordingly scaled up to the same level. Electricity consumptions were the product of the rated power, the working time and the scale-up coefficient.

Transportation distance (TRDS for short in Table 7.2) for auxiliary materials were measured and calculated based on producing regions and the help of Baidu™ electronic maps. Data at the background level such as raw material mining, environmental emissions and energy consumptions by transportations originated from Chinese Life Cycle Database. Table 7.3 summarises energy and material consumption data of two technologies, which were up-to-date data for the current technologies.

7.3.5 Hypotheses and Simplifications

Table 7.2 Data related with two cleaning technologies

Terms	**New technology**		**Conventional Technology**	
	SC-CO_2	LQB	THD	Shot blasting
Cleaning area	1.34 m^2		1.34 m^2	
Efficiency	26.8 m^2/batch		26.8 m^2/batch	
Gas	/	/	0 m^3	/
Water	/	4 g/cylinder	/	/
Ethanol	45.36 g/batch	/	/	/
Lime	Depends on the leaking rate of CO_2	/	Depends on CO_2 and SO_2 from fuel consumptions	/
$CaCO_3$	ibid	/	ibid	/
Ethanol TRDS	35 km	/	/	/
Lime TRDS	46 km	/	/	/
Diesel TRDS	/	/	46 km	/
Abrasive TRDS	/	32 km	/	32 km
Working time	30 min/batch	0.33 min/valve	10 h	8 min/cylinder
Attribition rate	4.38 kg/batch	0.036 kg/h	/	0.036 kg/h

Reasonable hypotheses and simplifications were made as follows, in case of unpredictable issues that could affect the accuracy and credibility of data procurement: a) fouling conditions on different valves were at an identical level; b) industrial SC-CO_2 cleaning used identical procedures as that at a laboratorial

scale; c) transportation for different materials used the same truck with capacity of 2 t.

Table 7.3 Energy and material consumptions for one function unit

Terms	**New technology**		**Conventional Technology**	
	SC-CO_2	LQB	THD	Shot Blasting
Water	2.87 g	0.4 kg	/	/
Ethanol	0.76 g		/	/
Electricity	11.07 kWh	0.88 kWh	0.4 kWh	0.995 kWh
CO_2	73 g		/	/
Ceramic balls	19.8 g		/	/
Diesel	/	/	5.6 kg	/
Steel shot	/		/	3.6 g

7.4 LCI Analysis

7.4.1 The LCI of the new technology

In supercritical CO_2 cleaning operations, electricity accounted for the major proportion of system input compared with that of other materials such as ethanol and water. Therefore, environmental impacts in supercritical cleaning are primarily from the consumption of electricity. Cleanliness from the two technologies should be identical to draw convincing conclusions for the life cycle assessment. Although researchers had proposed wetting methods for estimating surface cleanliness by measuring and calculating the contact angle between water and the metal substrates with the help of cameras and image processing software (Kuhn, 2005), there had not been widely accepted examining methods and corresponding cleanliness standards for cleanliness evaluation. Supercritical experiments in Chapter 6 has shown that 30 minutes residence time in the vessel was adequate to reach a similar cleanliness comparing with THD pre-treatment. SCF could extract about 50 g waste/contaminated diesel from contaminants in one function unit,

which therefore became a multifunctional process. A multi-functional process has impacts on more than one product system, and the environmental impact cannot be distinctively attributed to one specific system (Finnveden and Potting, 2014). To solve this problem, ISO 14044: 2006 states two hierarchical procedures, primarily based on subdivision, system expansion and allocation. Subdivision was not feasible in this case because supercritical cleaning per se was only one process; alternatively, substitution was employed to determine environmental impacts of the diesel "production", which subtracted corresponding materials of diesel from inventory of SC-CO_2 cleaning. Consequently, negative values were sometimes noticed on the SC-CO_2 life cycle inventory.

Table 7.4 Resources of consumption and pollution from different technologies

Pollution Category	**Pollution/ Resource**	**New Technology**			**Conventional Technology**		
		SC-CO_2	LQB	Total	THD	Shot BST	Total
Atmospheric emissions (kg)	CO_2	13.519	1.12	14.6	19.6	1.23	20.9
	CH_4	0.038	3.24E-03	4.17E-02	8.34E-02	3.54E-03	8.69E-02
	HCL	3.74E-03	2.99E-04	4.04E-03	2.98E-04	3.37E-04	6.34E-04
	HF	4.68E-04	3.75E-05	5.05E-04	3.72E-05	4.21E-05	7.92E-05
	SO_2	4.01E-02	3.26E-03	4.34E-02	3.66E-02	3.62E-03	4.02E-02
	NO*x*	3.79E-02	3.08E-03	4.10E-02	4.64E-01	3.42E-03	4.67E-01
	PM 2.5	1.57E-05	6.37E-05	7.94E-05	7.13E-04	1.16E-05	7.24E-04
	Inhalable particles	3.57E-05	3.71E-06	3.94E-05	3.22E-02	3.37E-06	3.22E-02
Water emission (kg)	Ammonia nitrogen	1.68E-05	2.97E-06	1.98E-05	1.18E-03	2.58E-06	1.18E-03
	Nitrate	1.93E-07	1.79E-07	3.71E-07	2.61E-06	4.83E-08	2.66E-06
	Phosphate	4.55E-07	4.09E-07	8.64E-07	9.24E-06	1.14E-07	9.35E-06
Resource consumption (kg)	Coal	8.96E+00	7.40E-01	9.70E+00	7.17E-01	8.10E-01	1.53E+00
	Natural gas	5.08E-03	4.73E-04	5.56E-03	1.05E-03	4.68E-04	1.52E-03
	Crude oil	-7.06E-03	1.40E-03	-5.66E-03	2.48	1.36E-03	2.48E+00

Water, electricity and abrasive ceramic balls composed the major input in the abrasive blasting system and were recycled during the cleaning operation. Nevertheless, there were always inevitable material loss during the swilling operations and between different batches. From the previous research, the attrition rate for LQB and shot blasting was regarded as 0.036 kg/h (Liu, 2010).

7.4.2 LCI of conventional technology

The heat for the degradation of contaminants was provided by the consumption of fuels, which was usually diesel, contained compounds of Sulphur and Nitrogen. Diesel accounted for a great proportion among the overall input of the THD cleaning; it was thereby the main resource of the environmental pressures by releasing oxides of C, S and N released into the atmosphere, along with particle pollution. However, most factories had paid little attention on the emission of these products; the inventory for THD cleaning was therefore analysed based on direct emissions into the atmosphere without any further treatment. By contrast, the environmental loads from the shot blasting process was much smaller, which can be credited to the lower demands for energy during the operations. Shot blasting used steel balls as abrasive materials in this process and was powered by air compressors. Therefore, the terms taken into consideration in the inventory were primarily from the manufacturing of steel balls and consumption of electricity. For the overall resource consumptions and pollutions, one can refer to Table 7.4.

7.5 Life Cycle Impact Analysis

LCIA aims at investigating the product system from an environmental

perspective, by use of the inventory obtained from the previous phase and providing information for successive interpretation phase in LCA. This phase comprises three mandatory elements: classification, characterisation and evaluation. The ultimate goal of this chapter is to evaluate the environmental pressure of the newly proposed cleaning method, compared with that of the conventional method. Accordingly, the results from LCI were categorised into five impact types: potentials for global warming (GWP), water eutrophication (WEP), acidification (AP), resource depletion potential (RDP), and respiratory inorganics (RI). The former three potentials are the common concerns all over the world, by researchers and governments. RDP was taken into the impact analysis as all the experiments were carried out in China the data cited are from a Chinese database. Moreover, the method would be probably promoted in China once the technology is well-developed for industrial use. Considering the hotspots about smog weathers reported by the media in China, especially in the north-eastern regions, RI becomes an indicator with great significance.

Characterisation process quantifies the contribution of different terms in LCI to the environmental impact potentials. potential calculations involved conversions of different factors into uniform and standardised values, by multiplying the emission amount with its corresponding equivalence factors, as depicted in Eq. (7.1), where Q represents the quantity of emissions or resource consumed, EF was corresponding equivalence factors and EP was the environment potentials. Subscript i and j represented the resource and impact categories, respectively. For this calculation, the EFs for global warming (GWP), water eutrophication (WEP), acidification (AP), resource depletion potential (RDP), and

respiratory inorganics (RI) were based on IPCC2007, CML2002, CML2002, ISCP2010 and IMPACT2002+, respectively.

$$EP(j) = \sum EP(j)_i = \sum \left[Q(j)_i \times EF(j)_i \right] \tag{7.1}$$

Normalisation of the impact potential indicators were essential to provide a reference that make the comparisons between different impact categories accessible. This LCIA used the per capita basis to calculate the normalised reference value, by dividing the environmental impact with corresponding population, as depicted in EQ. (7.2), where $NR(j)_{2010}$ represented the normalised reference on per capita; $EP(j)_{2010}$ was the global/regional environment potential; POP_{2010} was the global/regional population in 2010.

$$NR(j) = \frac{EP(j)_{2010}}{POP_{2010}} \tag{7.2}$$

Table 7.5 Reference values and weighting factors

Impact indicators	Characterisation equivalency type	Reference value (kg eq/(person·a))	Weighting factor
GWP	kg CO_2 eq	7857.5	0.174
AP	kg SO_2 eq	27.2	0.103
RDP	kg ce	11532.6	0.203
WEP	kg NO_3 eq	0.28	0.112
RI	Kg PM2.5 eq	11.9	0.078

Normalisation of the data can give the value of different environmental potentials. However, the environmental impacts of two different products may not be the same even if their environmental potentials are at a same value after the normalisation calculation. Therefore, the significance of different impacts is arranged by weighted evaluation process, where the assignment of studied impact

categories was implemented. The weighting factors, which are summarised in Table 7.5, were obtained by analysing questionnaires distributed to experts who attended the 2nd Chinese Life Cycle Management Conference. Results of the normalised LCIA are demonstrated in Table 7.6.

Table 7.6 LCIA results summary of different technologies

Impact indicator	Resource emission	Mass (kg)		Charact. factors	Potentials		Normalisation	
		New	Old		New	Old	New	Old
GWP	CO_2	5.939	20.87	1	6.38	23.1	8.12E-4	2.94E-3
	CH_4	0.017	0.087	25				
	N_2O	9.14E-5	1.96E-4	298				
AP	Ammonia	2.45E-5	3.29E-5	1.88	0.031	0.368	1.16E-3	1.36E-2
	HCL	1.65E-3	6.34E-4	0.88				
	HF	2.06E-4	7.92E-5	1.6				
	H_2S	5.34E-5	4.07E-5	1.88				
	NO_2	6.52E-5	2.18E-4	0.7				
	SO_2	0.018	0.040	1				
	NOx	0.017	0.467	0.7				
RDP	Coal	3.968	1.527	1	3.61	67.05	3.13E-4	5.81E-3
	Natural gas	2.31E-3	1.52E-3	12.8				
	Crude oil	-0.015	2.481	26.4				
WEP	Ammonia	4.89E-7	1.18E-7	0.35	1.65E-6	4.00E-4	5.79E-6	1.41E-3
	Nitrogen	7.72E-9	1.33E-7	0.42				
	Ammonia nitrogen	2.65E-6	1.18E-3	0.33				
	Nitrate	2.50E-7	2.66E-6	0.1				
	Phosphate	5.72E-7	9.35E-6	1				
RI	Particles PM2.5	7.91E-E05	7.24E-4	1	1.48E-3	2.11E-2	1.24E-4	1.77E-3
	Inhalable particles	1.65E-5	3.22E-2	0.536				
	Ammonia	2.45E-5	3.29E-5	0.121				
	NO_2	6.52E-5	2.18E-4	0.127				
	SO_2	0.018	0.040	0.078				

Fig. 7.2 gives the intuitive comparison of the normalised environmental indicators of two different technologies. Five indicators all smaller in the scenario that the new cleaning technology is used, with maximal reduction of up to 99.59% (in terms of WEP). After weighting, the environmental impact of new technology is $EI_{New}=3.34\times10^{-4}$, one magnitude less than that of the conventional technology

with the value of EI_{Old}=3.38×10^{-3}. The environmental impacts of respective methods in two technologies are 3.31×10^{-3}, 2.69×10^{-4}, 7.09 ×10^{-3} and 6.53×10^{-3} for THD, SC-CO_2, shot blasting and liquid blasting. Apparent results have demonstrated that the new technology possesses more environmentally friendly properties than the conventionally utilized THD and shot blasting.

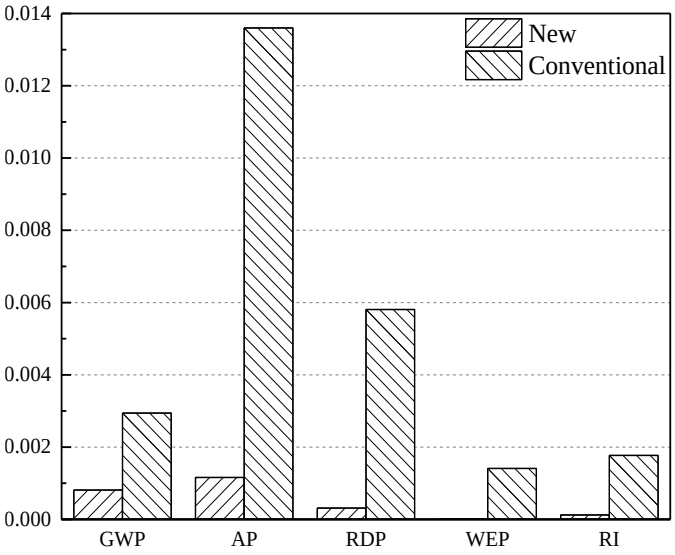

Fig. 7.2 A bar chart for indicators of two cleaning method after normalisation

7.6 Life Cycle Interpretation

The goal of life cycle interpretation stage is to analyse the LCA results, draw conclusions, interpret research limitations and provide systematic reports for the LCA in an explicit manner, based on the results from previous phases. ISO 14043 has listed the three crucial stages in the interpretation, including 1) identification of significant issues; 2) evaluation process for completeness, sensitivity and consistency checks and 3) drawing conclusions, stating limitations and giving recommendations. Through these steps, life cycle interpretation provides a series

of conclusions and recommendations for the study.

7.6.1 Significant Issue Identification

Data summarised in Table 7.4 demonstrated that pre-treatments in the two cleaning technologies are both the major contributors of material consumptions and pollutant emissions. In the supercritical CO_2 treatment, electricity accounted for a very large proportion of energy consumptions, which consequently dominated the environmental stress in the pre-treatment operation. The experiment was carried out in the northeast region in China. In this area, electricity majorly derived from thermal power plants that rely on consumptions of hard coal, whose exploitation and production consumes massive non-renewable resources, along with emissions of greenhouse gases such as CO_2, CO, NO_x and SO_2 during combustions. Notwithstanding the efforts that had been made in desulphurisation and HCL control during coal combustion, gaseous pollutants were still inevitable in thermal power plants. However, results could be much different if pre-treatment was operated in the southern region in China because the electricity in this region is primarily generated from hydropower, which is considered as an “greener” energy resource. Therefore, the energy resource alternation is required to replace conventional technology.

The THD cleaning expends 150 kg diesel in one batch of decomposition; comparatively, very little electricity is consumed in this process. Therefore, the combustion of diesel becomes the greatest pollution and emission resource, resulting in a considerably load of environmental pressures. The production of diesel also comprises the exploitation non-renewable resources like crude oil,

exacerbating the environment pressure from THD operation. In addition, the exhausted gases emitted in this process has gone through rarely treatment for current industrial utilisation, which leads to serious particle pollutions (PM 2.5) to the operators and the atmosphere. Consequently, factories using THD cleaning attempt to exploit alternative approaches and energy resources to overcome these drawbacks by, for instance, changing diesel into other "green" energy resource like natural gas.

It can be concluded from Table 7.4 that two post-cleaning operations possess much less environment impact within the corresponding cleaning technologies because they had small quantity of input and output in the system. The LCI result, however, is only valid in this study since the eventual impact results may vary according to the equipment power and the cleanliness requirement in actual operations. Previous studies have indicated that dusts produced during shot blasting can be detrimental to operators (Balan, 2008), even if the objects are enclosed by isolation structures in the blasting apparatus. By introducing water into the blasting system, atmospheric pollutions can be significantly reduced and dust particles are scoured with the flowing liquid into the draining structure. Therefore, liquid blasting has better environmental performance than the conventional shot blasting.

Carbon dioxide, the non-toxic and easily accessible gas, is recycled in the SC-CO_2 system with very little emissions and almost no noxious gases into the atmosphere. Yet, the combustion of organic materials in THD cleaning is a problematic issue requiring further means to decrease its environment impact. In addition, surface properties of products after THD treatment have usually changed,

such as hardness decrease phenomenon in Chapter 6. These results can additionally prove that SC-CO_2 cleaning (new cleaning technology) has the potential in becoming a promising "green" cleaning technology for the future industrial utilisation.

7.6.2 Contribution Analysis

As illustrated in Fig. 7.2, the conventional cleaning method had GWP of 23.10 kg CO_2 equivalency, which was approximately 2.6 times greater than that of the new cleaning technology. In the conventional cleaning, CO_2 emissions were majorly from the combustion of diesel that provide heat for contaminant decompositions in the THD cleaning process, accounting for about 97.2% in overall CO_2 emissions. The combustion of each kilogram diesel generates 3.41 kg CO_2 in the THD process. When it comes to the new technology, electricity is the primary contribution of GWP, accounting for 94.3% with 1.32 kg CO_2 equivalency in each kWh electricity use.

Normalised results demonstrated the AP of conventional technology was much greater comparing with the value of the new one, with the impact potential value of 0.368 and 0.031 kg SO_2 eq., respectively. The elements such as Sulphur and Nitrogen in crude oils cannot be completely removed during petrochemical production and transformed into oxides in diesel combustion, contributing to almost 99.1% of the AP in conventional technology.

Diesel production involves a series of refining processes of crude oil, which is non-renewable resource. The impact potential of diesel is calculated as 11.71 kg ce. for each unit. Comparatively, electricity generated in the northern region of

China significantly depends on the consumption of hard coals, with the impact potential calculated as 0.85 kg ce. per unit electricity generation. Main contributors for both methods were the consumption of energy resource, i.e. diesel and electricity, respectively, up to over 99% to RDP.

WEP has the least normalisation values in both technologies since electricity and diesel both emit very small amount of NH_4^+, NO_3^-, PO_4^{3-} etc. The consumption of each kWh electricity and kg diesel emits 8.57×10^{-7} and 7.06×10^{-7} kg PO_4^{3-} eq. from cradle to gate. Similar with the other potential terms, the energy input into the system was also the most significant factors that accounted for 95.2% and 99% to the respective technology.

In terms of RI, the condition was similar with that of AP. The normalization results of two technologies are calculated as 1.48×10^{-3} and 2.11×10^{-2} kg PM2.5 particles equivalency. The energy input into the system, electricity and diesel for respective methods, contribute more than 98% and 99% in the corresponding technologies in this potential term.

7.6.3 Sensitivity, Completeness and Consistency Checks

Sensitivity check evaluates the reliability of results from previous phases and determine the effects of the results induced by the variations in data collection, and allocation, irrational calculation methods and the hypotheses and simplification that have been used in the study. Eq. (7.3) gives the mathematical model to quantify the impact of the input variables on the output results.

$$S_{mn} = \left(\Delta O_m / O_m\right) / \left(\Delta I_n / I_n\right) \quad (7.3)$$

where O_m is the quantified values of environmental impact through calculations; I_n is the original data; ΔO_m and ΔI_n are the variations of O_m and I_n, respectively. S_{mn} demonstrates the sensitiveness of O_m with the change of I_n.

Sensitivity check was conducted on the auxiliary materials in the new cleaning technology, to evaluate sensitiveness of these materials by the scale-up speculation. Single factor check was used and the results are shown in Table 7.7. The auxiliary materials had very little effect on the final results of the impact potentials of indicators. The maximum influence was observed the impact of ethanol on RI, which was only 0.36%. Water, however, had almost no impact on the final results. It can be therefore concluded that the scale-up assumption used for the LCA is reasonable, with very little impact on the sensitiveness of indicators.

Table 7.7 Sensitivity check for auxiliary materials

Impact indicators	Water	Ethanol
GWP	0.00%	0.04%
AP	0.00%	0.02%
RDP	0.00%	0.16%
WEP	0.00%	0.14%
RI	0.00%	0.36%

Within the system boundary for respective cleaning technology, the data collected to meet the requirement are all available and intact. The major input into the system, i.e. the materials and energy consumptions has been included in the completeness check. Data for energy consumptions and material inputs of the SC-CO_2 cleaning process were obtained via reasonable scale-up of the laboratory. The other data of the direct input of the two technologies were collected from the

remanufacturing factories and the auxiliary data used the database of professional software.

Consistency check aims at determining that whether the assumptions, methods, models and data are dependable through the life cycle or among different schemes. In this study, the data were collected from different resources; for instance, primary direct input were obtained from factories and upstream data were obtained from professional database. Although the inconsistency of the data collection was inevitable considering the physical truth, the data collected can still guarantee the accuracy and reliability of representations because they were the first-hand data from factory and laboratory and the background data obtained from CLCD could reflect the current situation of the remanufacturing market in China.

7.7 Summary

The demand of "green" development in remanufacturing and external pressures for environmental benign approaches are the impetus for exploiting new methods for sustainable manufacturing. This chapter has used LCA method to evaluate the environmental impact of the newly proposed technology (SC-CO_2 pre-treatment + liquid blasting cleaning) and conventional cleaning technology (THD pre-treatment + blasting cleaning). Study focused on five primary environmental indicators namely GWP, AP, RDP, WEP and RI. Results of the normalisation for the five indicators demonstrated that the new cleaning technology had less environmental impacts than conventional methods. The comprehensive impact score for the new technology was 0.34×10^{-4} while the score of conventional method was 0.38×10^{-3}, which was approximately ten times greater

than the conventional technology. Therefore, the cleaning technology proposed in this thesis possessed more environmentally friendly features.

Through the independent analysis of each cleaning method in two cleaning technologies, the comprehensive environment performances of each method were scored as 3.31×10^{-3}, 2.69×10^{-4}, 6.53×10^{-5} and 7.09×10^{-5}, respectively for THD, SC-CO_2, shot blasting and liquid blasting. The score for one cleaning technology has a close relationship with its energy resources based on the analysis of this chapter: electricity and diesel consumptions are the primary factors inducing environmental pressures in the respective technologies. Pre-treatment processes, in both technologies, primarily determine the overall environmental impacts by controlling the energy input and consumptions. Consequently, by altering the energy input into environmentally friendly type could be a potential means to alleviate pollutions caused by the cleaning operation. From the technical perspective, increasing cleaning productivities is also promising method to promoting the use rate of energy; therefore, greener cleaning operations could also be achieved by optimising the cleaning operation and saving energy.

The LCA results from this chapter support the hypothesis that the SC-CO_2 cleaning could be greener in remanufacturing. To attain a similar cleanliness, the combination of SC-CO_2 treatment and liquid blasting has less impacts on the five crucial environmental indicators. However, the result in this study only represents a specific condition; more situations should be taken into consideration for more convincing results. Besides, the simplification in the goal and scope definition section may also increase the uncertainties of the study. Considering the high price of a SC-CO_2 device, what the preliminary LCA could provide is just a suggestion

that this new technology is a promising alternative for the cleaning of retired engine parts while more efforts are required for practical applications.

Chapter 8

Conclusions and Outlook

8.1 General Conclusions

In remanufacturing, cleaning is an important process of great demand, existing between other processes to guarantee the cleanliness of remanufactured parts and the quality of remanufactured products. Unlike OEM cleaning, remanufacturing cleaning confronts different types of contaminants and pollution degrees; therefore, it is difficult to achieve batched and automated production. In addition, cleaning processes are usually considered unfriendly to both the environment and human health due to the large amount of energy consumptions and emissions to the environment. The work presented in this thesis aims at finding an environmentally friendly or benign method to remove contaminants from decommissioned diesel engine component. The work is carried out parallelly on the investigation of cleaning technologies for OEM and contaminant in diesel engines.

Current industrially utilised cleaning technologies are summarised and the feasibility and pros and cons of cleaning technologies upon different kinds of contaminant are also concluded. Methods of cleaning, categorised into wet and dry cleaning, are either environmentally unfriendly, or have high equipment and operational costs associated. Utilising organic materials or other chemical removal

technologies, wet cleaning is thought to be problematic from an environmental perspective, as it involves various forms of more or less hazardous solvents and detergents. Further concerns arise from the energy consumption of the cleaning processes; there may also be risks associated with gaseous or fluid emissions, alongside the production of hazardous waste that needs to be treated with special care. Based on this, CO_2 is proposed as the cleaning agent that is possible to act as the environmentally friendly agent because CO_2 is easily accessible as a by-product of many industrial process. CO_2 has been used in cleaning process in forms of such as CO_2 snow and pellets. However, both the cleaning process are operated in an open condition, which could increase the green-house effect of the atmosphere. Therefore, CO_2 in the supercritical status is used as the cleaning agent (solvent), not only because of its inert properties, but also the unique characteristics of the supercritical status.

SC-CO_2 has the properties such as high dissolving ability, low toxicity, low surface tension and no residues remaining after operations. By regulating the pressure and temperature, a SCF can mimic the properties of different solvents; therefore, the SCF can be used to replace conventional solvents in chemical reactions. The adjustable density of a SCF makes it an excellent solvent for material removals and separations effortlessly. The first step for this application is to investigate the optimal parameters when handling a new type of substance. In most cases, the impact from parameters such as pressure, temperature, etc. are associated with each other; these parameters, especially temperature and pressure, are therefore optimised simultaneously to obtain the maximal removal effects.

A comprehensive understanding of the composition, structure, density and

thickness of the contaminant, on and inside the cores must be known, such as core materials, thermal stability, hardness and so on. Commonly the visible contamination can be categorised into five kinds: oily fouling; rusty fouling; scale; carbon deposition and paint layers. The thesis takes discarded engines as the cores to be cleaned. It can be usually observed that carbon deposition and greasy contaminants with hydrophobicity, high viscosity and high adhesive force. Oil and grease are common contaminants which can be easily found in the crankcase, on piston surfaces and cylinder heads, and on cylinder liners and fire rings. Carbon and Hydrogen are the major elements in contaminants, which accounts for more than 40% by weight and the EDS and EMPA analysis also detects the existence of other elements including Phosphorus, Sulphur, Aluminium and Zinc in the contaminants, which originated from the additives in the lubricating oil and the abrasion debris of the engine parts. The FTIR spectroscopy of the carbon deposition, oil contaminants and lubrication oil illustrates the broadly existence of saturated hydrocarbon bonds $(–CH_2–)_n$ in the contaminants. Based on the analysis, the proposal of using SC-CO_2 as the solvent could be a feasible approach in the removal of oily compounds from engine contaminants.

The study for the optimal parameters in the SC-CO_2 cleaning is based on experiments on lubricating oils and greases as the study objects. Experiments on the grease cleaning showed that the maximum removal rate could reach approximate 43% after cleaned in SC-CO_2 for 2.5 hours operated at pressure and temperature of 20 MPa and 70°C, respectively. Residues on the sample bases solidified with opaque appearances, which means that the internal structure of the contamination layer have changed in the SC-CO_2 fluid circumstance. More

specific studies are carried out on lubricating oils because they accounted for the major proportion in engine contaminants. Five crucial parameters were investigated and evaluated using single factorial experiments by used of oil absorbing pads as the carrier of contaminants. In the test range, the decontamination rate could reach over 90% and the positive impacts appeared in parameters of temperature, cleaning time and co-solvent mole fractions. However, the impact of temperature was more complicated. At a lower pressure range, the temperature presented a negative impact but it turned positive at a higher pressure. The competition effect from the temperature and pressure was especially obvious at the pressure ranging from 10 MPa to 22 MPa. Increasing the flow rate in the system could promote the dissolution of contaminants into SCF; however, the increment was extremely low. Based on the study, the optimal parameters for cleaning of lubricating oils are temperature between 55–75 °C and pressure between 20–30 MPa for 30–40 min cleaning durations with the addition of 7 mol% ethanol under the flow rate of 4–5 l/h.

For the further study on processing parameters, a mathematical model was established using the 2_{V}^{5-1} partial factorial experiment design. Results had shown that the temperature, pressure, their 2-way interaction and the co-solvent were the significant factors affecting the *CPI*. The model is sufficient to precisely predict the *CPI* influenced by the five parameters. Results showed that the *CPI* increased at higher temperature, higher pressure with dehydrated ethanol as co-solvent, and the optimal cleaning performance, calculated to be 89.30%, was obtained at 25.0 MPa, 75 °C. The optimal process parameters are highly recommended for processing heavily contaminated metallic engine components. SC-CO_2 cleaning is

an effective means for the remanufacturing cleaning process for automobile engines, with easy solvent recovery, low environmental impact and low life cycle cost. The only disadvantage of supercritical cleaning is the high pressure used in the cleaning vessel. Normally, equipment designed for elevated pressure is more expensive than that required for conventional chemical solvents.

According to the results from previous study, a new cleaning method is proposed, using SC-CO_2 as pre-treatment and LQB to remove the residues on engine parts and the comparison of cleaning real discarded engine components has been conducted between this new cleaning technology and the conventional method which combined THD and shot blasting as pre- and post- treatment process, respectively. The visible cleaning results shows that SC-CO_2 cleaning is an accessible approach for cleaning engine contaminants and more materials can be cleaned by the new method than by conventional technology. The carbon emissions were rarely observed during SC-CO_2 treatment because CO_2 was circulated with in the apparatus and SC-CO_2 had minimal the impact on surface properties while the hardness of components after THD significantly decreased.

To extend its application, another attempt is made in using the new cleaning technology to clean another kind of contaminant – paint coatings – which also broadly exist and are difficult to thoroughly clean from substrates. Experiments were carried out based on the artificially coated substrates that mimic the real paint layers on cores. Results confirmed that bubble nucleation dominates the mechanism of layer changes when specimens were soaked in SCF for a given dwelling duration. In contrast, no bubbles appeared on the surfaces of specimens who are treated without dwelling process (directly depressurised). Instead, cracks

were broadly generated on the surface of paints, which meant that the thermal expansion and contraction became the primary mechanism in this case. It was noted that bubbles in the paint layers would absorb the kinetic energy of the abrasive materials. Therefore, the dwelling procedures in fact had a negative impact on the cleaning results and should be avoided in the process. Paint fragments segmented by the cracks were lager in a higher SCF temperature and on a thicker layer. Subsequently, liquid blasting was used to clean the specimens from previous operations and the parameters were determined based on single-particle shot tests. Even when the impacting velocity is relatively low, paint layers could be still removed; increasing the impacting velocity or the diameter of the grit benefits the cleaning process, but higher velocities may also damage the surface of the stainless steel.

Based on the experiment investigations on loose (greasy and oily) and heavy (paints and coatings) contamination layers, SC-CO_2 cleaning, combined with other cleaning technology, is a promising alternative to conventional cleaning methods in commercial applications. Owing to its mild processing temperature, SC-CO_2 can be more extensively used in cleaning than THD, when the substrate materials are with low melting point such as aluminium.

Following on from the experiments, the LCA methodology is used as a scientific tool to evaluate its environmental performances and to compare with that of the conventional technology. The study focused on five primary environmental indicators, namely global warming (GWP), water eutrophication (WEP), acidification (AP), resource depletion potential (RDP), and respiratory inorganics (RI). The normalisation results of these indicators showed that the new method

had less impact on the environment than the conventional method. Comprehensive impacts of new technology scored 0.34×10^{-4}, one order of magnitude smaller than that of the conventional technology. Therefore, the new cleaning method proposed in this thesis had better environmental performance comparing with the conventional method. Independent analysis on each treating means in the two technologies revealed that the energy consumptions of pre-treatment processes (electricity and diesel consumptions for new and conventional technologies, respectively) are the primary resource of environment pressures. It is possible to enhance the environmental performances of the technologies by changing the energy input into "greener" type or increasing cleaning efficient. Therefore, it is possible to achieve a greener cleaning process by optimizing the cleaning process, increasing the cleaning efficiency and energy using rates. LCA results provide supportive conclusions for the hypothesis that SC-CO_2 is a "greener" solvent that could replace organic solvents and SC-CO_2 cleaning could be an alternative means for remanufacturing.

8.2 Research Outlook

This section presents limitations of the research demonstrated in this thesis and provides possible recommendations for further investigations surrounding SC-CO_2 applications in the cleaning industry. This thesis introduces some preliminary work on the feasibility of SC-CO_2 as a green agent to replace conventional solvents and propose new cleaning technologies for the engine remanufacturing industry. Numerous modifications and optimisations could be carried out surrounding this technology. It is noted that the work is only carried out at a laboratory level, which

could only clean a small number of cores and is usually both time and energy consuming. Increasing the cleaning efficiency is absolutely the ultimate goal for process optimising and technical optimisation because it could directly determine the energy and supply consumptions and economical performances of the technology. Other considerations regard to study from contaminant aspect and developing green additives for the process.

Firstly, although the cleaning technology proposed in this thesis could achieve the "greener production" for remanufacturing and it can be more broadly applied to cores with different substrate materials, post treatment is still an indispensable part to remove residues from SC-CO_2 cleaning and attain a satisfactory result. A better choice is to completely remove contaminants by integrating the post-treatment into SC-CO_2 cleaning. The possible means is to add mechanical agitations into the cleaning vessel or the SCF, such as adding magnetic stirring devices, ultrasonic generators or generating pressure pulses in the cleaning vessel. However, supporting facilities required re-designed, for instance the cleaning vessel. It is impossible to wire into the current vessel to provide electricity for ultrasonic generators or magnetic stirring devices. The vessel should be able to exchange energy (electricity in common cases) with the external environment and can maintain the designated pressure at the same time. SC-CO_2 PPC is another research direction. It has been reported that PPC is effective in remove particle contaminants from micro cracks and blind holes while no reports have been seen carried out on "open" contaminants. More parameters should be considered, such as the pressure amplitude, pulse frequency, substrate dimension and appearance. The pipelines and valves in the SC-CO_2 facility should be also redesigned to carry

out PPC as the pressure pulses are detrimental to not only contaminant but also the valves controlling the pressure changes.

The current SCF test rig is with an irrational tube-shaped cleaning vessel, which has inhibited its applicability on cores of different shapes. Further investigations could also be commenced on designing vessels that could control the fluid flowing and therefore flowing types over the contaminant layers. It would be a promising method to increase the material exchanging ability through controlling the flowing types over contaminants and ultimately the cleaning efficiency.

The results of this research have demonstrated the effectiveness of co-solvents in increasing effectiveness of oil contaminant cleaning although contaminants are not miscible in co-solvents like ethanol. It is not clear how co-solvent molecules interact with CO_2 and contaminant materials. Further investigations could be performed on the ternary system composed by SC-CO_2 fluids, contaminant materials and co-solvents using tools such as molecular dynamic simulations. The molecular simulation results may provide theoretical basis for exploring co-solvents with better dissolving ability and better environmental performances.

The results obtained from this work could be used as a fundamental work for proposing new projects. Future work from both the theory and application perspectives could provide solid background knowledge of contaminant dissociations, improving performances of the SC-CO_2 technology and promote its commercial utilisation in cleaning industry.

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Appendix A

Experimental Test Rig Details

Following on from the introduction from Chapter 4, the meters, indicators, valves, switches and parts has been specifically demonstrated in the images below. Fig. A-1 to 4 shows the functions of different cells: control panel, gauges, valves and system setup.

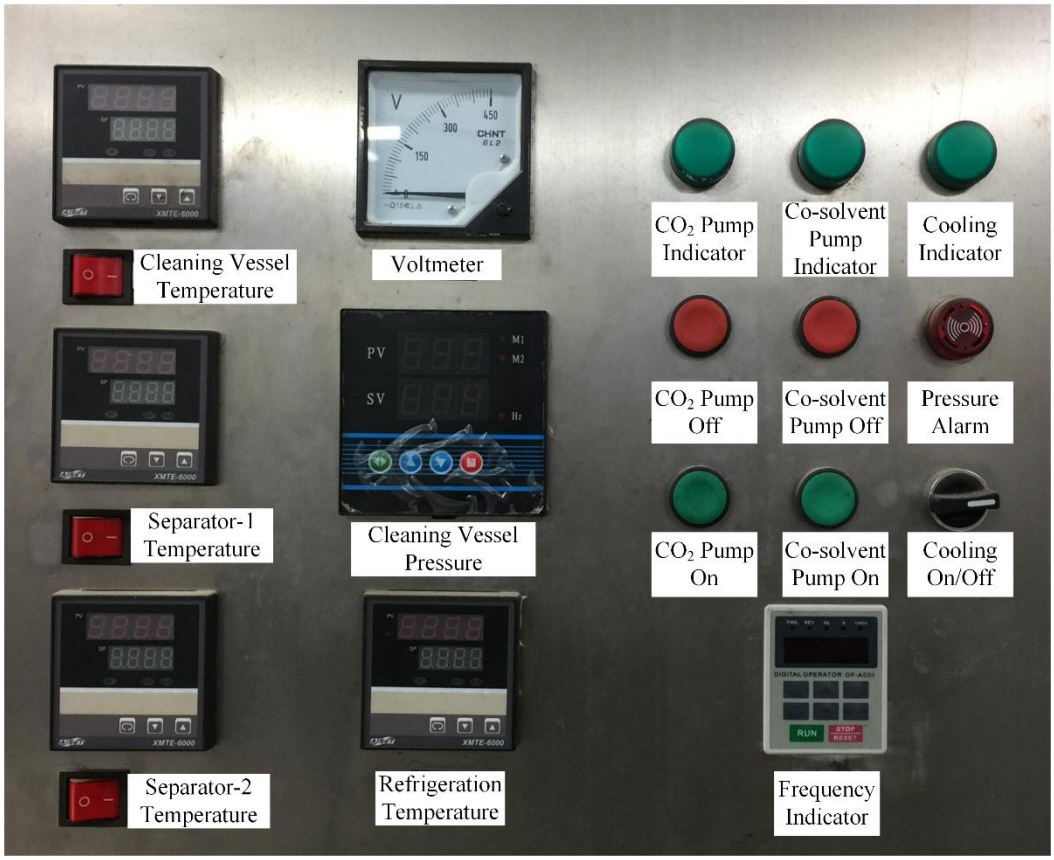


Fig. A-1 The control panel of SC-CO_2 cleaning test rig

Fig. A-2 Gauges of the SC-CO_2 cleaning test rig

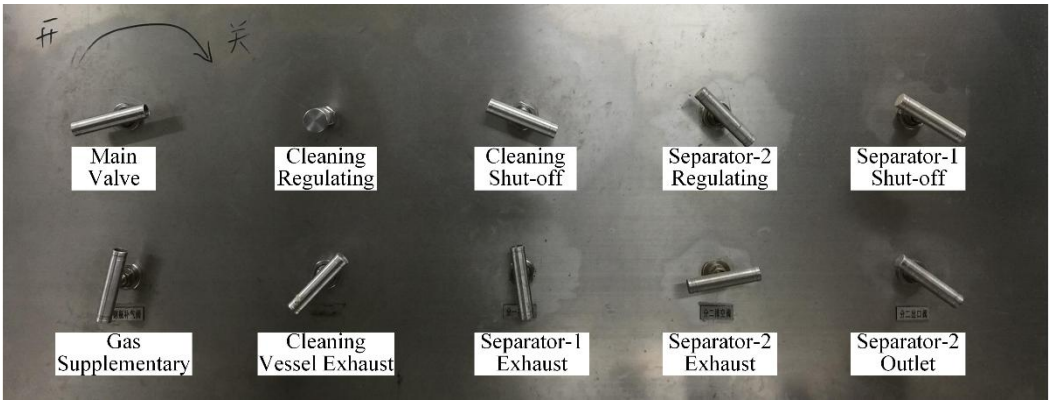


Fig. A-3 Valves in the SC-CO_2 cleaning system

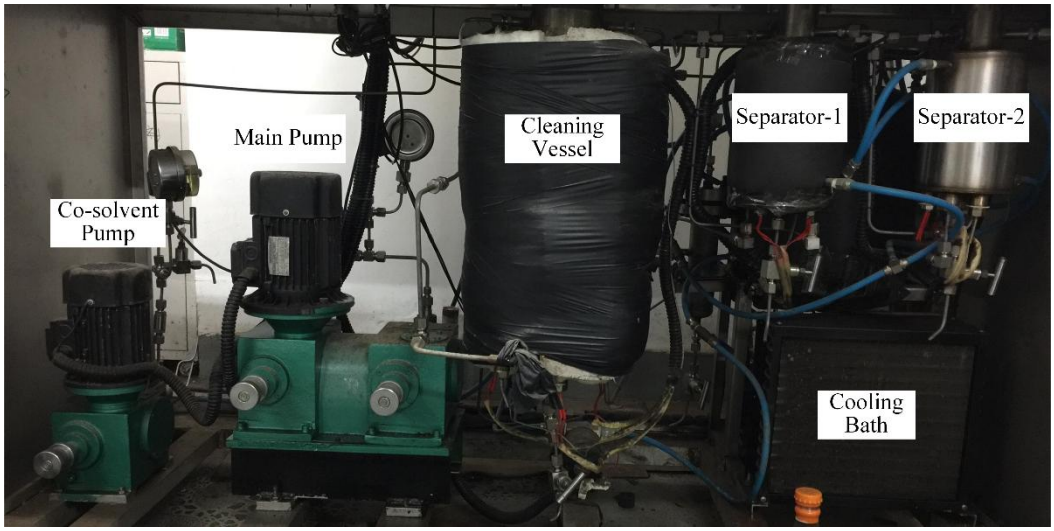


Fig. A-4 Demonstration of crucial component of the cleaning system

Appendix B

Experiment Data

The raw data from the cleaning process has been shown in this section, including the data of grease cleaning and lubricating oil cleaning experiments.

B.1 Original data of grease cleaning process

Table B.1 Experiment data of grease cleaning under different temperatures

T/°C	Net wt./g	Total wt./g	Remaining wt./g 0.5 h	1.0 h	1.5 h	2.0 h	2.5 h	3.0 h
50	28.7462	29.3542	29.1992	29.1858	29.159	29.1026	29.097	29.0943
	28.7067	29.4095	29.2269	29.2183	29.1858	29.1242	29.1193	29.1018
	28.6283	29.3784	29.1974	29.1688	29.1432	29.0757	29.0673	29.0601
60	27.8014	28.4196	28.2555	28.2082	28.1806	28.1645	28.163	28.1611
	28.0125	29.2853	28.9446	28.864	28.8066	28.7857	28.7721	28.7656
	27.9648	28.4361	28.3163	28.2722	28.2448	28.2409	28.2397	28.2362
70	28.7167	29.2739	29.1095	29.0619	29.0504	29.041	29.0384	29.0367
	28.7132	29.2987	29.1275	29.0861	29.0544	29.0485	29.0383	29.0357
	28.8445	29.3637	29.2089	29.1765	29.1547	29.1422	29.1363	29.1345

Table B.2 Experiment data of grease cleaning under different pressures

P/MPa	Net wt./g	Total wt./g	Remaining wt./g 0.5 h	1.0 h	1.5 h	2.0 h	2.5 h	3.0 h
15	28.8949	29.4621	29.3465	29.2594	29.2449	29.2387	29.2343	29.2334
	28.7468	29.5247	29.3656	29.2545	29.2281	29.2179	29.2057	29.2033
	28.5796	29.6372	29.4315	29.2682	29.2573	29.2301	29.2103	29.2098
20	27.8014	28.4196	28.2555	28.2082	28.1806	28.1645	28.163	28.1611
	28.0125	29.2853	28.9446	28.864	28.8066	28.7857	28.7721	28.7656
	27.9648	28.4361	28.3163	28.2722	28.2448	28.2409	28.2397	28.2362
25	28.7047	29.369	29.1663	29.1189	29.1063	29.0994	29.097	29.0946
	28.6843	29.2794	29.1068	29.0647	29.0524	29.0471	29.0455	29.0352
	28.6014	29.3045	29.0867	29.0438	29.0359	29.0284	29.0271	29.0236

B.2 Original data of lubricating oil cleaning process

Table B.2 Experiment data of lubricating oil cleaning under different pressures and temperatures[1]

A: Temperature=35 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0405	15.0158	11.7654	2.1655	15.2312	11.4059	1.9758	14.3912	11.4011
8.5	2.1032	14.9387	10.6085	2.2111	15.5888	12.3102	1.9302	13.0476	9.5666
10	2.0964	14.6504	7.766	2.1755	15.1845	8.4435	1.9423	13.3585	7.4257
14	2.1004	15.2182	7.0488	2.1267	14.6704	7.0582	1.9599	14.2768	5.9566
18	2.096	15.1975	6.4505	1.9285	13.5215	5.8793	2.0015	14.8133	6.1601
22	2.0571	14.6853	6.1018	1.9287	13.6109	5.8675	1.9396	13.9561	5.7474
25	2.0701	14.8079	6.0502	2.0716	14.4341	5.4002	1.9651	14.3925	5.5079
30	2.1854	15.2622	5.8503	1.9175	13.2554	5.3271	1.9531	14.4777	4.9565

B: Temperature=45 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0447	15.2669	12.7957	2.0883	14.7001	12.5031	1.6172	11.8163	9.8891
8.5	2.0840	14.4804	12.1022	2.1798	15.2894	12.7820	1.6831	11.395	9.7832
10	2.0887	14.8290	10.6585	2.1629	14.9479	10.4859	1.6675	11.3756	7.5038
14	2.0983	14.9460	6.0594	1.9036	13.2832	5.7112	1.6393	11.9624	5.3898
18	2.1976	14.9735	5.2353	1.9130	13.6671	5.2313	1.6131	11.9113	4.8446
22	2.0733	15.0165	4.8871	1.9040	13.5150	4.8958	1.6211	11.8193	4.3845
25	2.1400	15.0015	5.0938	1.9511	12.9406	3.6946	1.6388	11.9254	3.6269
30	2.0483	15.2869	4.4865	1.9356	12.3706	3.8072	1.6772	11.4525	3.4673

C: Temperature=55 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0854	14.6106	12.6613	1.9293	13.6426	11.5076	1.8832	13.8970	11.8221
8.5	2.0516	14.6473	13.0435	2.2158	15.8744	13.6953	1.9392	14.0676	12.4312
10	2.0367	15.0002	12.2228	2.0786	14.203	11.4435	1.9205	13.9622	10.6923
14	2.0720	14.8571	8.0016	2.1542	14.9433	7.9721	1.8831	13.0783	7.0012
18	2.0688	14.7050	5.2456	2.1785	14.9319	5.0417	1.8716	13.0488	4.5116
22	2.0906	15.2585	5.6028	1.9505	13.3071	4.1036	1.8833	13.0018	4.2623
25	2.1039	14.7907	4.4041	2.1901	14.9565	4.4497	1.9027	14.1256	4.1499
30	2.1645	15.8153	4.6574	2.1797	15.261	4.5180	1.9080	14.1627	4.0127

1. In Table B.2, m_0, m_1 and m_2 denotes the mass of original oil absorbing pads, the mass of pads prior to cleaning and after SC-CO_2 cleaning, respectively.

D: Temperature=65 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0904	14.5599	12.2816	1.9702	13.7985	12.0172	1.9112	14.0699	12.1165
8.5	2.0825	14.6681	13.1782	1.9987	14.3102	12.5426	1.8323	13.3369	12.1345
10	2.0782	14.0808	11.546	1.9923	13.8716	11.1402	1.8493	13.4817	11.0282
14	2.0411	13.6702	9.2238	1.9179	13.2961	8.8343	1.8444	13.3484	9.0599
18	2.0816	15.2278	5.4005	1.9856	14.0807	4.9179	2.0256	14.7491	5.2376
22	2.0753	14.1372	4.8434	1.9047	13.0597	4.2095	1.8237	12.6893	4.142
25	2.1018	14.7315	3.9008	1.9034	13.5328	3.806	2.0983	15.2979	4.1996
30	2.1757	15.5547	3.9107	1.9803	14.0197	3.5568	1.9126	14.018	3.3023

E: Temperature=75 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0863	14.5737	12.8755	1.7293	13.1537	11.5872	1.9136	14.0762	12.5665
8.5	2.0498	13.6707	12.6325	1.7101	13.409	12.1225	1.9609	14.5093	12.8172
10	2.1032	14.8216	13.0131	1.7719	13.7115	11.8159	1.9042	12.7367	11.1411
14	2.0639	14.2543	10.5299	1.7382	13.1755	9.8056	1.9348	13.0387	9.6194
18	2.0673	14.0656	7.0585	1.6797	12.7182	6.3968	1.9278	12.7635	6.5509
22	2.0793	14.6279	4.9516	1.7853	13.7653	4.6213	1.9527	13.0558	4.3286
25	2.0957	14.3732	3.6866	1.758	13.5908	3.1915	2.0036	14.3266	3.4373
30	2.1858	15.3429	3.7758	1.7469	13.2593	3.2128	1.9736	14.1836	3.3900

F: Temperature=85 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.116	14.5235	13.29	1.8119	13.2053	11.7781	1.9047	13.1235	11.9628
8.5	2.0792	14.5115	13.3327	1.8169	13.1035	11.5547	1.8962	13.2958	11.8905
10	2.0567	14.2534	12.4929	1.8795	13.2706	11.3076	1.8898	13.2801	11.2039
14	2.0572	14.1581	11.4645	1.8252	12.6822	10.0851	1.9037	13.6749	10.8345
18	2.0802	14.4064	8.0173	1.9363	13.6118	6.884	1.9007	13.6621	7.1237
22	2.0701	14.3756	4.933	1.9369	12.8869	4.8028	1.9101	13.861	5.2537
25	2.0476	14.0232	3.6004	1.8866	12.7635	3.0536	1.9236	13.8321	3.5658
30	2.1561	15.1133	3.9049	1.8413	12.8165	3.0634	1.9045	13.5639	3.3627

G: Temperature=95 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0076	13.9252	12.7393	1.7306	11.8753	10.3843	1.9775	13.2248	11.6252
8.5	2.0248	14.6522	12.7595	1.7562	12.4652	10.7319	1.942	13.0583	11.1951
10	1.9949	14.6325	12.7468	1.7641	12.6621	10.9014	1.9767	14.5821	12.3875
14	2.0257	14.7215	11.4337	1.7913	12.7184	10.2083	1.9656	13.4653	10.3915
18	2.0342	14.4151	8.9585	1.7477	11.8406	7.5994	1.9619	13.3571	8.5921
22	2.0297	15.102	5.5158	1.7582	11.9313	4.4544	1.9397	12.885	4.9794
25	1.9978	14.7634	3.6252	1.7461	11.7643	2.5956	1.9443	12.8918	3.0561
30	2.1336	15.1354	3.2865	1.7557	11.941	2.4244	1.9605	13.3906	2.6328

H: Temperature=105 ℃

P/MPa	Replication 1			Replication 2			Replication 3		
	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g	m_0/g	m_1/g	m_2/g
7.5	2.0504	14.2553	13.2941	1.6208	11.9944	10.527	1.647	11.6352	10.4409
8.5	2.0226	14.3126	13.2145	1.6568	11.384	9.8532	1.6534	11.7174	10.1984
10	2.037	14.1663	12.0355	1.6574	11.5759	9.9744	1.6989	11.3548	9.6266
14	2.0438	14.6203	11.8467	1.6474	11.5973	9.3272	1.6413	11.1578	8.9432
18	2.0268	14.2737	9.7056	1.6623	11.2381	7.7864	1.6072	11.9578	8.1184
22	2.0299	14.547	5.5391	1.634	12.0095	4.1825	1.6015	11.7801	4.4365
25	2.0345	14.2843	3.8858	1.5981	11.8984	3.2707	1.6650	11.4605	3.3394
30	2.056	14.9375	3.5202	1.6201	11.4769	2.2149	1.5983	11.8107	2.3068

Appendix C

Cleaning Results by Different Methods

Appendix C shows figures of all samples that were cleaned by the comparative experiment between different cleaning method combinations in Table 6.1 in Section 6.2.

Fig. C-1 Recovered samples from retired engines, prior to being cleaned (a) – Tappet, (b) – Tappet interior, (c) – Tappet top, (d) – Rockshaft, (e) – Cylinder bolt, (f) – Nozzle, (g) – Rocker arms, (h) – Valve

Fig. C-2 Samples after SC-CO_2 pre-treatment

Fig. C-3 Samples after test No. 1 in Table 6.1: SC-CO_2 followed by abrasive water jet cleaning

Fig. C-4 Samples after test No. 2 in Table 6.1: SC-CO_2 followed by ultrasonic cleaning

Fig. C-5 Samples cleaned by thermal cleaning

Fig. C-6 Cleaned samples of test No. 3

Fig. C-7 Cleaned samples of test No. 4

Appendix D

Microscopic View of Paint Layers

This section illustrates all the images of paint layers in Chapter 6, taken by ultra-depth and ordinary microscopies, including the paints treated after SC-CO_2 treatment, single shot blasting tests and after liquid blasting operations.

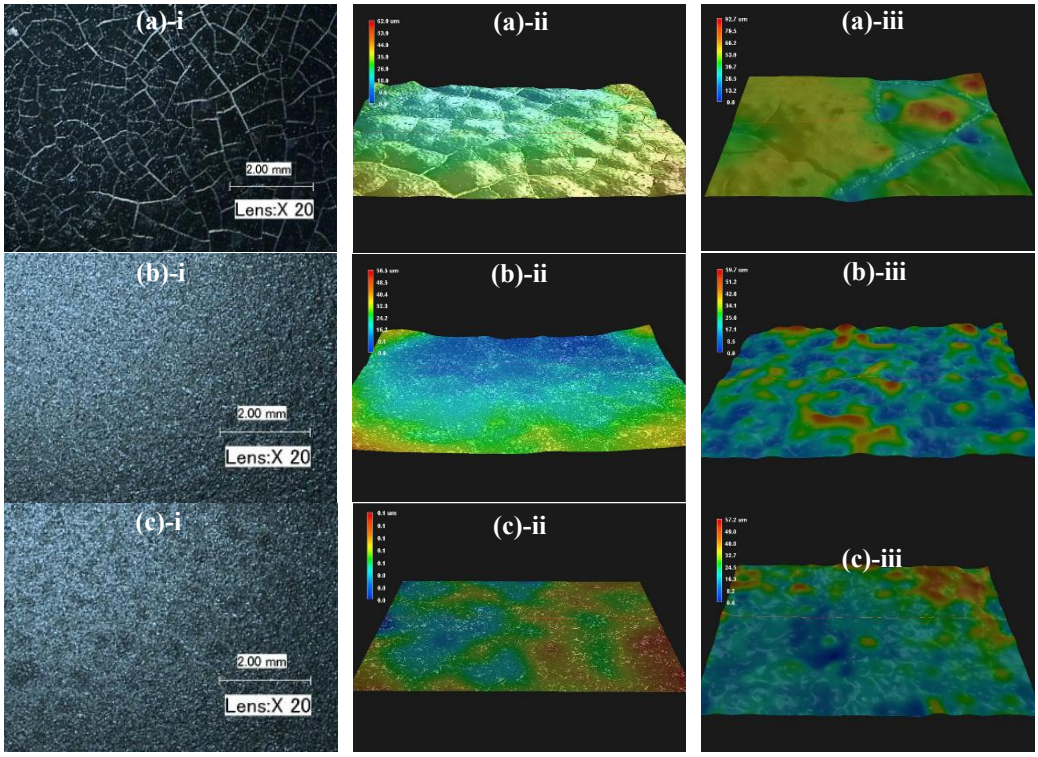


Fig. D-1 Images of paint layers under different dwell durations in an SCF[1]; (a) – 0 h, (b) – 1 h, (c) – 2 h

1. In this section, the numbers i, ii and iii denote that the images were shot under magnifications of 20 times, 100 times and 200 times, respectively.

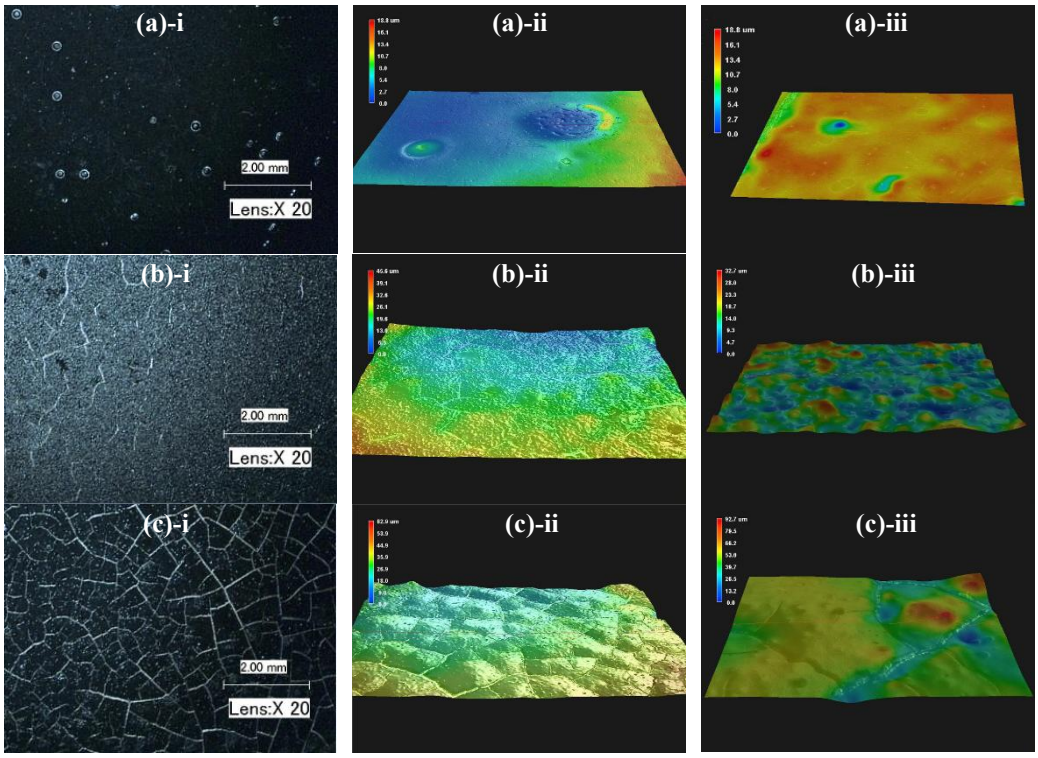


Fig. D-2 Images of paint layers under different pressures in an SCF; (a) – 10 MPa, (b) – 15 MPa, (c) – 25 MPa

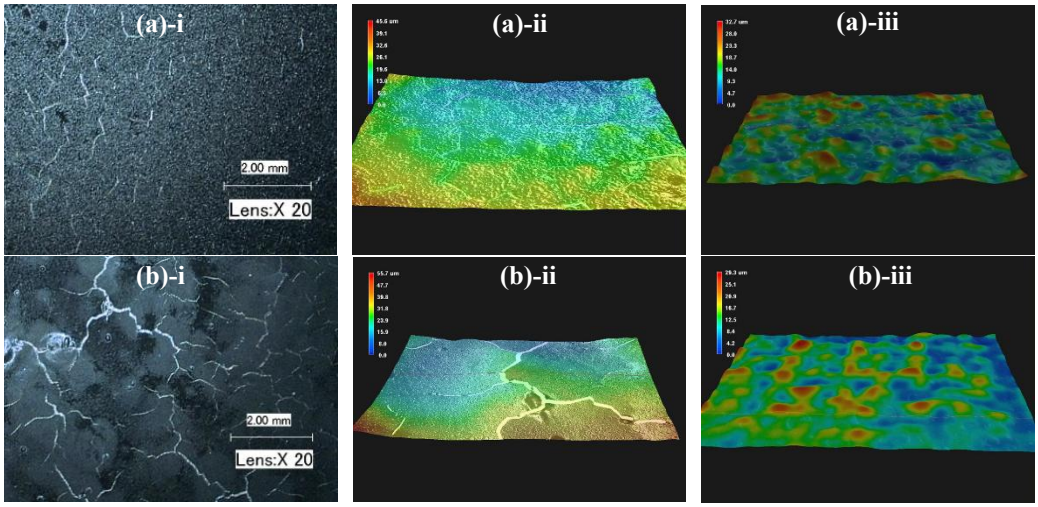


Fig. D-3 Images of paint layers under different temperatures in an SCF; (a) – 40 °C, (b) – 60 °C

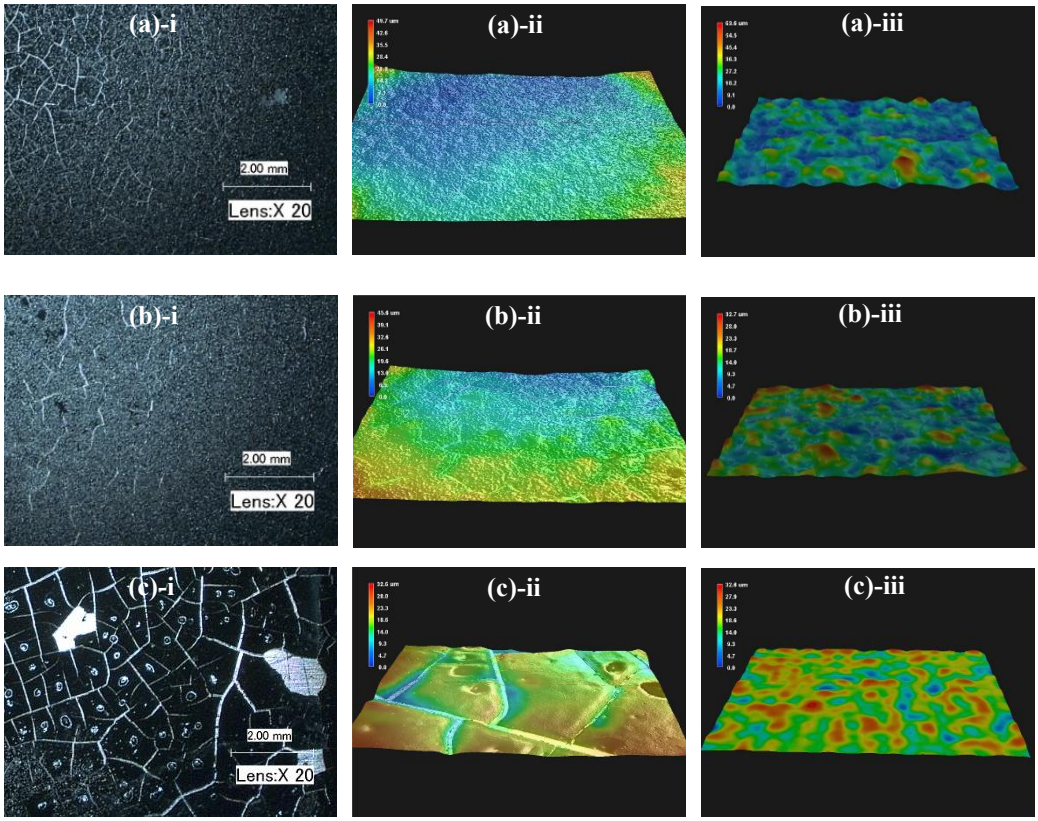
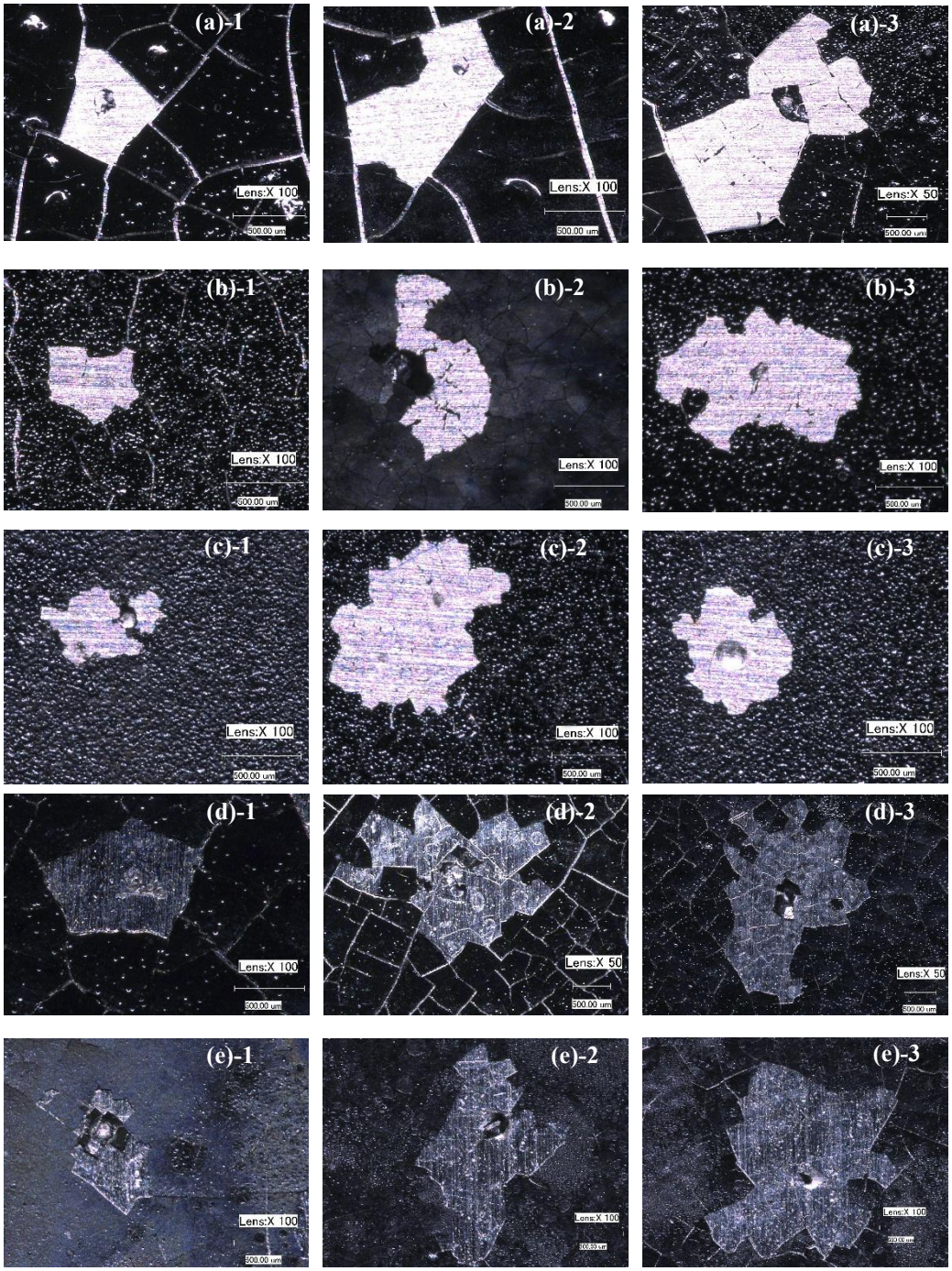


Fig. D-4 Images of paint layers under different paint thickness in an SCF; (a) – 0.06 mm, (b) – 0.1 mm, (b) – 0.2 mm


(a)-1
Lens:X 100
500.00 um
(a)-2
Lens:X 100
500.00 um
(a)-3
Lens:X 50
500.00 um
(b)-1
Lens:X 100
500.00 um
(b)-2
Lens:X 100
500.00 um
(b)-3
Lens:X 100
500.00 um
(c)-1
Lens:X 100
500.00 um
(c)-2
Lens:X 100
500.00 um
(c)-3
Lens:X 100
500.00 um
(d)-1
Lens:X 100
500.00 um
(d)-2
Lens:X 50
500.00 um
(d)-3
Lens:X 50
500.00 um
(e)-1
Lens:X 100
500.00 um
(e)-2
Lens:X 100
500.00 um
(e)-3
Lens:X 100
500.00 um

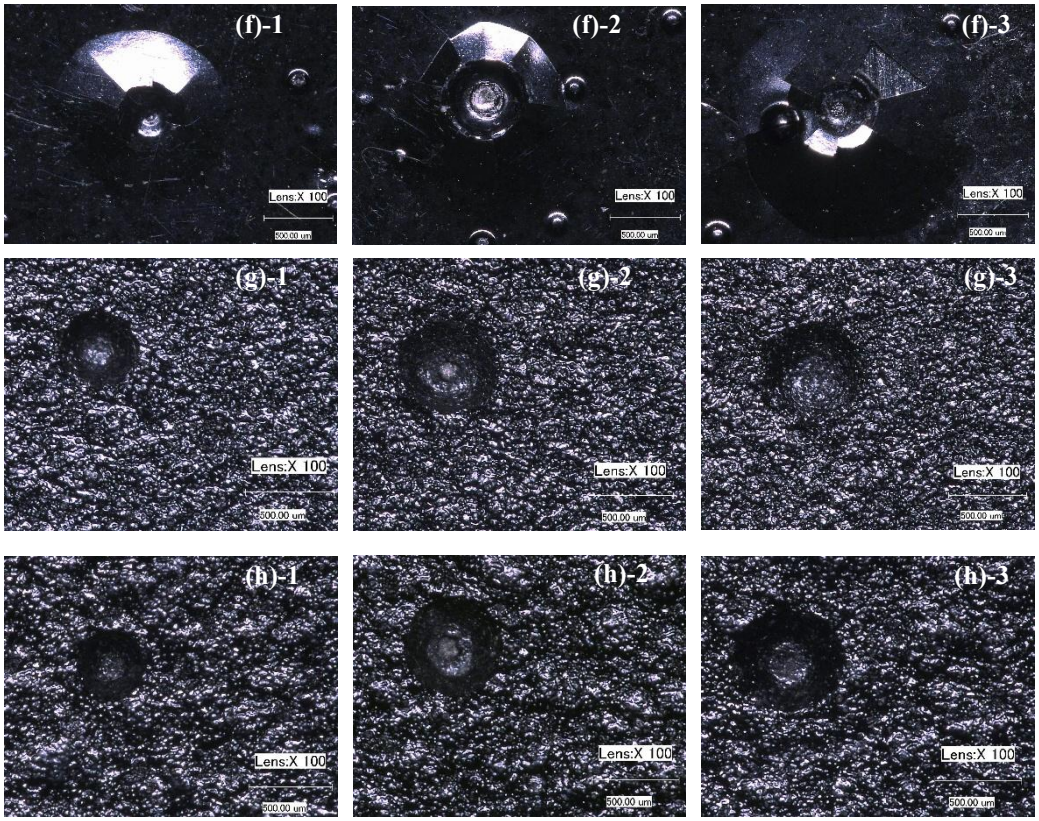


Fig. D-5 The morphology of paint layer shot by single-particle blasting under different parameters[2, 3, 4]

2. Pre-treatment parameters for each row are as follows:
   a: 15 MPa, 40 °C, 0h, 0.2 mm; b: 15 MPa,40 °C, 0h, 0.1mm;
   c: 15MPa, 40 °C, 0h, 0.06mm; d: 25MPa, 40 °C, 0h, 0.1mm;
   e: 15MPa, 60 °C, 0h, 0.1mm; f: 10MPa, 40 °C, 0h, 0.1mm;
   g: 25MPa, 40 °C, 1h, 0.1mm; h: 25MPa, 40 °C, 2h, 0.1mm.
3. Propelling pressure and particle diameters in each column are:
   1 – 0.2 MPa, 0.3 mm; 2 – 0.4 MPa, 0.3 mm; 3 – 0.2 MPa, 0.9 mm.
4. (a) – 3, (d) – 2 and (d) – 3 are under the magnification of 50 times; the other images are under the magnification of 100 times.